Final Report

Evaluation of Reverse Osmosis for Brackish Groundwater Desalination at Gilroy and Hollister, CA.

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Executive Summary

The Stanford Department of Civil and Environmental Engineering and the Santa Clara Valley Water District (SCVWD) evaluated the feasibility of desalinating brackish groundwater using reverse osmosis (RO) at two sites in the inland basin of the Pajaro River Watershed. Two RO pilot systems were built and deployed, one on the premises of the South County Regional Wastewater Facility near the towns of Gilroy (Gilroy site), and the second site was adjacent to the Domestic Wastewater Treatment Plant of the City of Hollister in San Benito County (the San Benito site). The overall goal was to identify potential issues that might affect full-scale implementation of RO technology for groundwater desalination. The towns of Gilroy and Hollister are located, east of the coastal range, approximately 30 air-miles from the Monterrey Bay. Specific project objectives included: (1) designing and building two pilot RO systems deploying, (1) testing and evaluating the systems at two different sites for brackish groundwater sites; (3) gaining operational experience; (4) investigating membrane fouling processes; and (5) studying the presence of organic wastewater indicator compounds in groundwater and their removal by RO treatment. Concurrently, we studied a novel technology to mitigate membrane fouling by applying protective coatings to membranes. The latter study supported by the National Science Foundation and executed in collaboration with Membrane Technology, Inc. (MTR, Menlo Park, CA). The results of this work of thas been published elsewhere (Louie et al. 2006 and Louie, 2008).

The two identical RO unites were designed for producing 15 gpm permeate flow. The units were equipped with 6 pressure vessels arranged in a 2:1 two-stage configuration; each pressure vessel was equipped with 3 brackish membrane elements (M-T4040AHF, Applied Membranes, Inc., Vista, CA). The Gilroy RO unit was operated at a water recovery of 83% (STD ± 1.6%) and reduced TDS levels from 770 mg /L in the feed to approximately 11 mg/L in the permeate, corresponding to an average salt rejection of 98.4% (standard deviation (STD) ± 0.22%). The San Benito RO unit was operated at 81% (STD ± 2%) water recovery and reduced the TDS from an average of 1227 mg/L in the feed to 59 mg/L in the permeate, corresponding to an average salt rejection of 95% (STD ± 0.8%). At both sites, the groundwater showed a relatively strong scaling tendency. Deposition of calcium-magnesium carbonates, silica and biomass were suspected to be the factors governing membrane fouling.

Evaluating conceptual groundwater desalination systems that included extraction, desalination, and brine management RMC recommended desalination with a water recovery of 83% to minimize brine management expenses. The study summarized here indicates that 83% water recovery is feasible, although not optimal when RO operation is considered in isolation.

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1. Introduction

Population is growing rapidly in Santa Clara Valley as in much of California and the American Southwest. As a result, the demand for fresh water is growing while at the same time natural supplies remain constant and the threat of severe droughts due to climate change is increasing. Hence, there is a significant need to develop alternative water supplies. One potential source that is being considered is to desalinate brackish groundwater. Groundwater supplies are central to the water supply strategy of many water districts. In Santa Clara County, nearly half of the water used is supplied by local aquifers (Reymers and Hemmeter, 2001), and salination of even a small fraction of the aquifer capacity represents a significant economic loss. In the San Francisco southbay region, salination of groundwater has occurred in several places, including, for example, in Alameda County adjacent to the San Francisco Bay where seawater has intruded into aquifers because of over-pumping and in southern Santa Clara County where treated wastewater effluent has infiltrated into aquifers either from ponds or as a consequence of irrigation with treated effluent.

Reverse osmosis (RO) is one of a limited number of options to desalinate water and to produce fresh water. RO involves forcing water across a water-permeable membrane that rejects dissolved salts. The RO process is relatively energy, capital, and maintenance intensive. Typically RO systems require site-specific optimization, i.e., design and operation depend on the quality of the feed water, brine disposal options, and the intended use of the product water. RO also removes a wide range of other contaminants, including organic solutes, colloids and particles. RO is therefore often used to polish reclaimed water so that the product water can be blended with potable water supplies.

The salts and the other contaminants that are removed by RO are concentrated in the brine. Unless this waste stream can be properly disposed of, application of RO is not possible and therefore not a solution to the water shortage problem. When evaluating brine disposal options, both the flow and its salt content must be considered. The salt content of the brine increases as the fraction of water recovered increases; conversely its volume decreases as water recovery increases. For example, increasing recovery from 50 to 87.5 % increases the salinity in the brine from two to eight times of the salinity in the feed water. On the other hand, increasing water recovery decreases the brine flow by a factor of four (from 50% to 12.5 % of the feed), thus potentially facilitating brine disposal. In evaluating the feasibility of different brine disposal options, many factors need to be considered, the most important one being the distance between the project site and an environmentally acceptable coastal outfall. At inland sites where ocean disposal of brine is not an option, the alternative approaches may be expensive or environmentally unacceptable and prevent application of RO altogether. There are few alternative brine disposal options at inland sites and all are relatively unattractive: discharge to sewer systems, various brine concentration techniques, injection into deep wells, or evaporation to dryness followed by landfilling of the salt residues. Ocean disposal also requires consideration of environmental impacts, especially in the vicinity of marine sanctuaries, such as the Monterey Bay.

The number of published reports on desalinating brackish groundwater is limited and the practice appears relatively rare. For example, the Alameda County Water District

(ACWD) commissioned a study to evaluate desalination as a means to augment local supplies and to remediate portions of an aquifer that has become brackish (McKee et al. 1999). The coastal aquifer used by the ACWD as a water supply has become brackish because of saline water intrusion from the San Francisco Bay. To expand local supplies, the ACWD is extracting and desalinating brackish water, which it then blends with fresh groundwater to produce high quality water. A pilot study commissioned by the ACWD achieved 97 % TDS rejection and a permeate TDS concentration below 100 mg/L. The concentrate composition was within discharge requirements. Since then, the ACWD has built a 5 MGD RO plant, which has been in operation since 2005 and is used to augment potable supplies.

In a year long study, the Marin Municipal Water District (MMWD) evaluated brackish San Francisco Bay water desalination using advanced treatment (Kennedy/Jenks, 2007). This program studied the specific challenges of treating Bay water as the feed and developed a basis for "a comprehensive evaluation of a full-scale facility." The Kennedy/Jenks (2007) study concludes "seawater desalination of Bay water can be a viable, reliable, and drought-proof drinking water source for Marin."

The productivity, sustainability, maintenance costs, and energy demand of RO treatment is affected by numerous factors, including the salt content in the feedwater, the presence of precipitating salts (scalants), and water contaminants that adhere to or precipitate onto the membrane (foulants). The combined total of all processes that diminish the performance of the membranes is termed *fouling*. Fouling can be mitigated by pre-treating the feed for the removal of foulants, e.g., removal of particulates and bacteria by microfiltration. Other pretreatment steps may include addition of chelating agents to the feed stream, which keep cations such as Ca^{2+} in solution and prevents the precipitation of insoluble $CaSO_4$, or water softening to remove Ca^{2+} and Mg^{2+} altogether. The expected cause of fouling during the desalination of groundwater is precipitation of insoluble inorganic phases that are naturally present in the aquifer in a dissolved state but are concentrated beyond saturation by the RO process. The most common cause of scaling in brackish water operations is precipitation of insoluble salts, such as calcium sulfate, calcium carbonate, barium sulfate, and silica.

Selection of treatment chemicals and cleaning solutions, and performance optimization all require site-specific evaluations. Duranceau et al. (2003) for example, conducted a study to explore ways to enhance the performance of a full-scale plant at City of Sarasota, located on the Gulf Coast of Florida. The plant was treating raw water with a TDS of 2,180 mg/L, 880 mg/L sulfate, 3.4 mg/L sulfide, and a total hardness of 1,175 mg/L**.** They evaluated scale inhibitor type, water recovery, and pH on hydraulic performance and fouling behavior. Calcium sulfate scaling was significant when acid treatment was employed. Typical cleaning procedures using citric acid, caustic or EDTA/Borax/TSP were not effective in removing the calcium sulfate scale.

RMC (2007) studied the technical and economic feasibility of producing 3,000 AFY fresh water by desalinating 1,800 mg/L TDS San Juan basin groundwater in Hollister, CA. RMC considered options for groundwater extraction and conveyance, desalination, and concentrate management. The recommended system includes three-stage RO and blending the product water with a small fraction of untreated groundwater followed by

decarbonation. For brine management and disposal, RMC recommended brine concentration by the Vibratory Shear Enhanced Process (VSEP), discharge of the concentrated brine to an evaporation ponds and landfill disposal of the residual salts. The target water quality after blending was 300 mg/L TDS. In the overall scheme, brine management and disposal is the most expensive component: 66% of the capital project costs and 75% of the overall operating costs would be spent for brine management. Ocean disposal was not competitive even though the project is located relatively close to the coast (approximately 50 miles). For estimating the overall treatment costs, the water recovery of the RO process was assumed to be 83%. The cost estimates for consumables, energy, labor and chemicals totaled $430,000 annually.

Typical costs at inland desalination facilities are approximately $2.3 to $3.6 per 100 cubic feet of water produced (New Mexico Water Resources Research Institute, 2004). The RMC recommends a scenario for the San Juan basin that includes brine concentration and salt landfilling, consistent with inland applications, i.e., without the possibility of ocean disposal. RMC estimates that the costs for producing 3,000 AFY fresh water from groundwater with a TDS of 1,800 mg/L costs approximately $2,200 per AF or $5 per hundred cubic feet produced (including the costs associated with groundwater extraction, desalination treatment, concentrate management and product water distribution) (RMC, 2007). The estimated accuracy of this estimate is +50 to -30 percent and therefore consistent with the range of typical costs indicated by the New Mexico Water Research Institute earlier (2004). This study validates the approach recommended by RMC although operational experiences suggest that scaling problems would likely increase the estimated operation and maintenance (O&M) and energy costs.

Belkacem et al. studied the fouling of RO membranes during the desalination of groundwater in a pilot system (Belkacem et al. 2007). These authors operated their system at 75 % recovery for 12 months. They observed better than 95% salt removal (measured as conductivity) and a 10% flux decline during 20 weeks of operation. The flux decline (or the membrane resistance) increased exponentially, and they suggested that the rate of fouling was controlled a by precipitation reaction. Analysis of the cake layer indicated a deposit of a mixture of gypsum (calcium sulfate) and calcium carbonate.

The potential for scaling can be predicted based on geochemical calculations that consider the presence of insoluble salt forming ions in the feed water, specifically the degree of super-saturation of insoluble salts, the ionic strength, which is dependent on composition and type of salts, the temperature, system configuration and recovery, and the membrane type. These calculations serve as the starting point for the design of RO systems and indicate the potential need for treatment chemicals. Many factors are difficult to predict, however, especially biological fouling and fouling by soluble and particulate organic matter. Various fouling phenomena cannot be considered in isolation and therefore require site specific testing. For instance, microbial fouling can be complicated by the addition of antiscalants that support biological growth substrates. Pilot tests of sufficient length are recommended to study the fouling potential of specific waters. Water quality of groundwater may change, leading to different fouling phenomena. Pilot tests of short duration may not reveal problems that become evident only after months or years of operation. The RMC study evaluated the precipitation of

minerals was studied for a specific groundwater sample (#63367) as a function of water recovery. The study found that in the absence of an antiscaling agent a water recovery of 75% would result in significant saturation effects for calcite and aragonite. At approximately 83% recovery, their modeling suggests that the concentrate would also be supersaturated with respect to hydromagnesite.

This report is organized as follows: after this introduction, we describe the investigative approach, which is followed by sections describing the analytical methods, and results of the pilot tests, membrane autopsy, and economic considerations. Finally, we summarize conclusions, recommendations and the references. Additional details on the design, execution, results, and photographs are given in the appendices.

2. Project Rationale

The Santa Clara Valley Water District (SCVWD) is charged with maintaining, protecting, and restoring the quality of its groundwater supplies. This study was undertaken to obtain preliminary information on the feasibility of desalinating brackish groundwater with RO at sites two sites in the Pajaro River Watershed. Two study sites were selected, one located on premises of the South County Regional Water Control Plant (SCRWQCP) and one in adjacent to the Hollister Waste Treatment Plant (HWTP). Groundwater salinity was caused by wastewater effluent that was used to irrigate crops or leaked from treatment ponds or sewer lines and infiltrated into the groundwater. Additional goals of this study included the investigation of the presence of organic wastewater indicator compounds in the groundwater and their removal during RO. The information generated in this study will help planning groundwater remediation projects and evaluate the viability of brackish groundwater desalination as a potential water source.

The Pajaro River Watershed is maintained by three primary water management agencies, the San Benito County Water District (SBCWD), the Santa Clara Valley Water District (SCVWD) and the Pajaro Valley Water Management Agency (PVWMA). To coordinate their efforts, these agencies established the Integrated Regional Water Management (IRWM) program. The study reported herewas executed in conjunction with "The Pajaro River Watershed Groundwater Desalination Feasibility Study," which is a planning effort by SBCWD and SCVWD. It aims to identify the technical, economic and institutional benefits and barriers to implementing groundwater desalination in the Pajaro River Watershed (RMC, 2007).

This project was funded by the SCVWD and the California Department of Water Resources and was executed in a partnership between the Stanford University and the Santa Clara Valley Water District (SCVWD). The two pilot plants used for the study were designed in collaboration with and built by Applied Membranes Inc. (AMI, Vista, CA). In conjunction with this study, we conducted research on fouling mitigation by protective coating. That research was supported with funds from the National Science Foundation and executed in collaboration with Membrane Technology, Inc. (MTR, Menlo Park, CA). During the course of this work, we developed a methodology to improve fouling resistance of membranes by coating membranes with a permeable polymer (Louie et al. 2006 and Louie, 2008)). The field component of this research was

executed at the Gilroy site after the "Process Evaluation Phase" during the "Fouling Study Phase."

3. Project Objectives

The objectives of this study were to assess the feasibility of RO for brackish groundwater desalination in the Santa Clara Valley and to identify potential issues that might affect full-scale implementation of RO technology. Specific goals of the project were to:

1. Design, build, deploy, test and evaluate two pilot RO systems for brackish groundwater desalination at two different groundwater sites;
2. Gain operational experience at two brackish groundwater sites;
3. Investigate membrane fouling processes;
4. Study the presence of organic wastewater indicator compounds in groundwater and their removal by RO treatment.

4. Metrics for Success

We defined success of this project by the following criteria: Did we

1) Gain information that is useful for evaluating the feasibility of full-scale RO for brackish groundwater desalination?
2) Identify critical site–specific issues that might be relevant for operating full-scale RO systems at these sites?

The project was successful in that (1) the technical feasibility of groundwater desalination at the two sites was demonstrated, and (2) technical recommendations for more detailed process optimizing studies at these sites were developed, and (3) information was developed that can be used evaluate published scenarios (RMC, 2007) for implementing RO as a groundwater desalinization technology in the Pajaro River Watershed.

5. Project Approach

5.1. Site selection

Two sites were selected: the first site was situated on the premises of the South County Regional Wastewater Facility in Gilroy (the Gilroy site) and was identified by the SCVWD in July 2005; the second site was adjacent to the Domestic Wastewater Treatment Plant of the City of Hollister in San Benito County (the San Benito site) and was identified in March 2006 (Figure 1).

At Gilroy, the RO system was installed on firm soil next to the clarifying basin with easy access from the road. At San Benito, installation was in an open field approximately 100 yards from the road. Both sites were operational in October 2006.

5.2. Regulatory and monitoring requirements

Salts measured as total dissolved solids (TDS) are covered under the Environmental

Protection Agency's National Secondary Drinking Water Regulations (EPA, 2003). The secondary drinking water standard for total dissolved solids (TDS) is 500 mg/L and water with a TDS of 700 – 850 mg/L is often unfit for irrigation, but this threshold can be as low as 500 mg/L depending on the type of crops that are irrigated. In general, water with TDS over 1,000 mg/L is considered brackish or saline and problematic for both industrial and agricultural use.

For the discharge into the San Benito River, the Central Coast Regional Water Quality Control Board required continuous automated monitoring of TDS and pH reported as hourly averages, and weekly monitoring for turbidity, alkalinity, dissolved organic carbon, and concentrations of specific ions, as well as daily average discharge volumes.

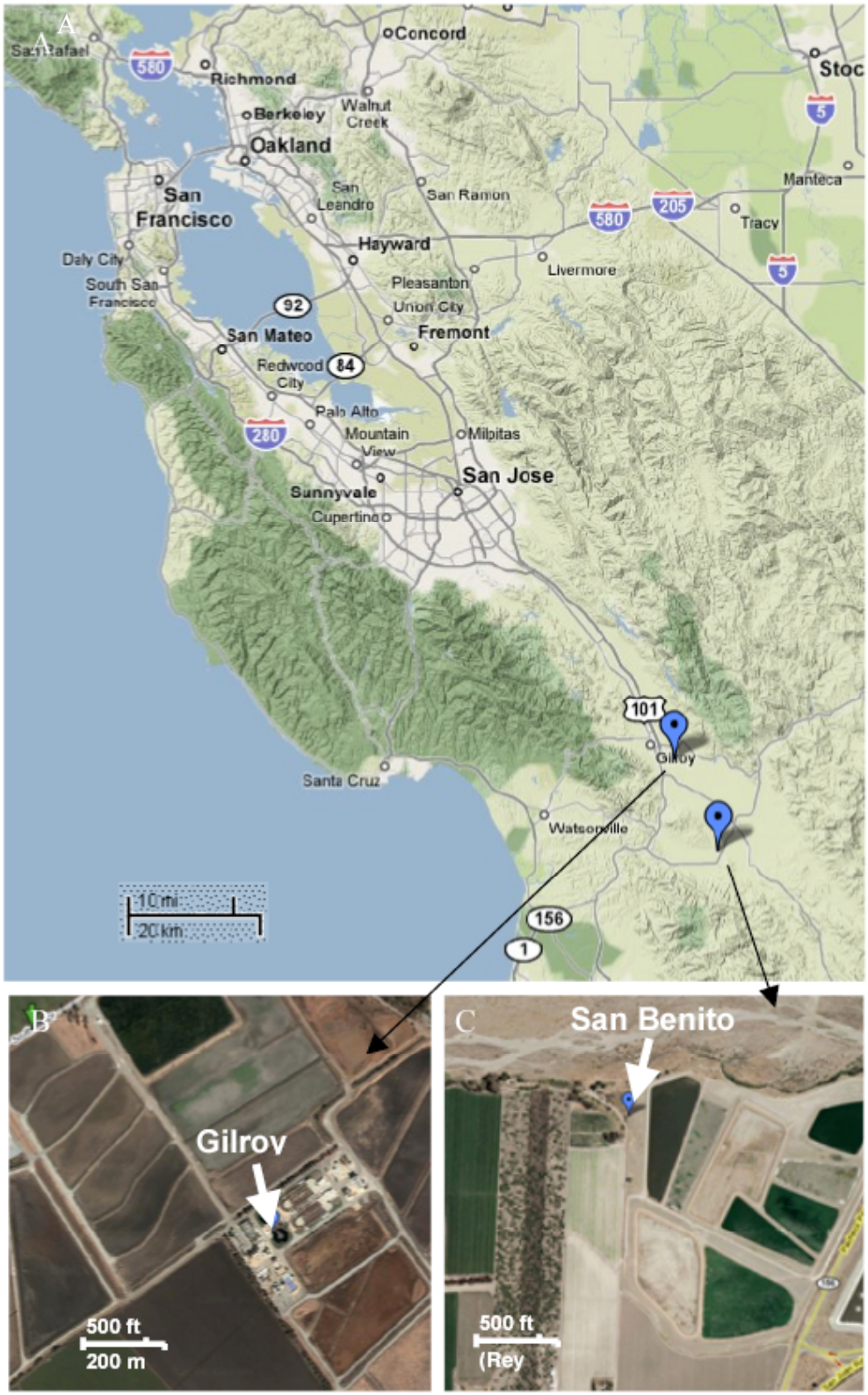


Figure 1. Location of the two RO pilot systems. A: Bay Area with Santa Clara Valley. B: Gilroy site with the South County Regional Wastewater Facility and recharge basins. C: San Benito site with San Benito River bed (source: Google maps).

5.3. Design of RO units

5.3.1. System design and construction

Proposals to build two pilot systems were obtained from AMI, Vista, CA 92081 and Harn RO Systems, Inc., Venice, Fl 34292. The proposal from AMI (Appendix A) was consistent with the budgetary constraints of the project, and it was decided to work with AMI. Figure 2 shows a basic schematic of the RO pilot systems. A schematic of the system and the parts list is given in Appendix B and photographs of the Gilroy system are given in Appendix C.

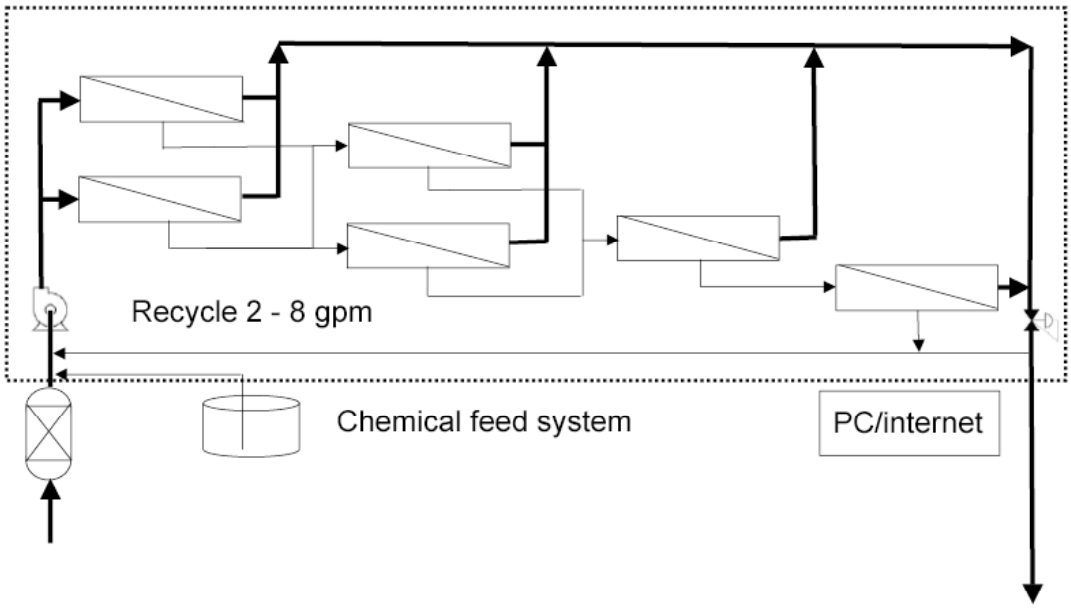


Figure 2. Simplified schematic of the RO pilot unit (A schematic of the systems is given in Appendix B).

The array shown above represents a two-stage system in a 2:1 configuration, with the first stage consisting of two parallel trains of two pressure vessels in series and the second stage consisting of a series of two pressure vessels. Each vessel housed three 4-in. x 40 in. elements rated to 300 psi operating pressure. The concentrate streams of the first two pressure vessels were combined and the configuration may be designated as a (2:2):(1:1) array. The design permeate flow was 15 and the system was equipped with a recycle loop that was adjustable from 2 and 8. This design allowed simulation of a full-scale 2:1 membrane configuration with full-scale vessels holding six elements each.

Typical operation involved pumping groundwater from the wells through the cartridge filter, amending the feed with antiscalant, blending with the recycled retentate, followed by pumping the blend into the first stage using a high-pressure pump that was controlled by a variable frequency drive. Permeate and concentrate were combined prior to being discharged into the clarifying basin (Gilroy) or spraying over an open field within the San Benito riverbed (San Benito).

Flow rates and pressures were controlled by manually adjusting valves. The feed flow control valve was located after the high pressure RO pump, the ratio of permeate flow to the concentrate flow was controlled by another valve and the recycle flow was controlled by a third valve on the concentrate discharge flow stream. For performance monitoring, pressure gauges and flowmeters were installed at various locations in the system. Sampling ports allowed collection of samples for water quality analyses. A laptop computer was used for system control and on-line data acquisition.

The major system control functions were for:

- System start up and shut down
- Pressure alarms
- Chemical pump level and shut down
- System faults, alarms, and status

The following parameters were acquired continually with sensors connected to the data system:

- **Temperature, pH and conductivity:** feed, permeate, concentrate
- **Flow:** feed, permeate, concentrate, recycle stream
- **Pressure:** pre and post cartridge filter, post high pressure pump, concentrate, permeate

Two filters encased in polypropylene corrosion-proof housings suited for brackish water conditions were used to remove particulates in the feed water supply. Each housing contained a 20 in. long 4.2 in. diameter polypropylene cartridge rated at a nominal 5 microns pore size.

The antiscalant (Flocon 260, AMI Vista, CA) was fed from 50-gallon inert plastic tanks, and a chemically inert positive displacement pump was used to inject the antiscalant into the feed supply water. The system was also equipped for the addition of sulfuric acid, although this system was not used at either site.

5.3.2. Design specifications

Table 1 summarizes the key features of the pilot system, Table 2 provides a summary of the parameters used as the design basis, and Table 3 indicates the specifications of the RO elements provided by AMI.

Table 1. RO System Performance Specifications

Feed Flow	Membrane	Membrane array	Recycle
Permeate 15	4 in. dia x 40 in. long M-T4040AHF (AMI)	Nominally 2:1 6 housings in (2:2):(1:1) array 3 elements/housing	Adjustable 2-8

Table 2. Design Basis

Water quality characteristic	Design	Recommended by manufacturer
Feed Water TDS	574	
Design Temperature	25 deg. C (assumed)	
Electrical	480 V, 3 HP, 60HZ	
Membrane Type	AMI 4x40 Thin film	
Feed (incoming) Water Pressure	40-60 psi	
Design Operating Pressure	185-250 psi	< 300 psi
Temperature Range	15 to 35 Deg. C.	< 45 Deg. C.
Feed Water Turbidity	< 1 NTU	<1 NTU
Feed Water Silt Density Index	< 3	< 4 (15 min)
Capacity Basis	24 hours/day. Continuous operation	

Table 3. Manufacturer's RO Element Performance Specifications

Model No.	Permeate Flow Gal/Day	Permeate Flow Liters/Day	Minimum Salt Rejection	Stabilized Salt Rejection
M-T4040AHF	2,800	10,598	98	99

These membrane specifications are based on 2000 mg/L sodium chloride, 225 psi (1.6 MPa) applied pressure, 77°F (25°C) feed water temperature, pH 8 and 10% recovery (element flow is expected to vary within ±15%). The chlorine tolerance is <0.1ppm, the specified pH range is 2-11 and for short term cleaning 1-12. The effective area of an element is approximately 400 ft^2.

5.3.3. Membrane Cleaning

A separate mobile cleaning unit was acquired consisting of a cleaning solution tank with a cleaning solution delivery pump, and control systems, which were mounted on a mobile skid. The system was designed to pump cleaning solution through the equipment in closed-loop mode. The cleaning solutions used were proprietary formulation by AMI and included AM-11 and AM-22. Product description, Material Safety Data Sheets, and cleaning protocols are given in Appendix D. Membranes were investigated for fouling deposits after completion of the test as discussed below.

6. Experimental Methods

6.1. Data Evaluation

System performance was evaluated in terms of salt rejection and water recovery. The salt rejection, R_{Salt}, is defined as:

$$R_{Salt}\ (\%) = (1 - (TDS_{Permeate} / TDS_{Feed})) \times 100 \quad (1)$$

The water recovery, W_R, is given be Equation 2:

$$W_R\ (\%) = (Flowrate_{Permeate} / Flowrate_{Feed}) \times 100 \quad (2)$$

Other parameters that were tracked over time and plotted included: the feed, permeate, concentrate and recycle flows, and pressure, TDS, and pH measured, respectively, in the feed, brine, and permeate. To maintain constant flow and to compensate for membrane fouling, the pressure was increased. The pressure increase was therefore evaluated as an indication of fouling.

6.2. On-line Sensors

The parameters shown in Table 4 were measured online.

Table 4. Physical and Chemical Parameters Measured On-Line

Parameter	Sample Locations Within System	Comment[a]
Flowrate[a]	Feed, permeate, concentrate, recycle	
Pressure	Influent, permeate, concentrate	
Temperature	In conjunction with pH and TDS	
Total dissolved solids (TDS)[c]	Feed, permeate and concentrate streams	Measured indirectly as electroconductivity
Electroconductivity	Feed, permeate and concentrate streams	Not reported, expressed as TDS
pH[a]	Feed, permeate and concentrate streams	

Note:

a — Flowmeters were recalibrated using a timed volume collection and were quite close (<5% error). An exception was the recycled flow where the original setting was off significantly. The initial offset probably led to problems early on with scaling at the San Benito RO unit;

b — The temperature and pH probes were not recalibrated, original manufactures settings were accepted;

c — TDS probe measurement was non-linear at high concentrations and affected by scaling.

6.3. Water analysis

6.3.1. General and Mineral Analyses

The parameters shown in Table 5 were measured periodically using the standard methods indicated.

Table 5. Standard Methods (SM) for General and Mineral Analyses

Characteristic	Method	DLR[a]	MCL[b]
Nitrate	EPA 300.0	2 mg/L	45 mg/L
Sulfate	EPA 300.0	0.5 mg/L	250 mg/L
Chloride	SM 4500 CI-D		250 mg/L
Turbidity	SM 2130 B		
Bicarbonate Alkalinity (as $CaCO_3$)	SM3220 B		
Carbonate Alkalinity (as $CaCO_3$)	SM3220 B		
Hydroxide Alkalinity (as $CaCO_3$)	SM3220 B		
Total Filterable Residue at 180 ^oC	SM 2540 C		
Dissolved Organic Carbon	SM 3510 C		
Calcium	EPA 200.7		
Iron	EPA 200.7	100 μg/L	300 μg/L
Magnesium	EPA 200.7		
Silica	EPA 200.7		
Sodium	EPA 200.7		

Note:
a — MCL: maximum contaminant level
b — DLR: detection limit for reporting

6.3.2. Trace Organics Analysis

The methods used to study trace organic contaminants target wastewater indicator compounds were the same as those used in a previous study (Gross et. al., 2003). A summary of the analytical protocol is given in an Appendix E along with the methods used of membrane autopsy.

6.4. Membrane Fouling Autopsy

6.4.1. Membrane sample collection and autopsy

Fouled membrane elements were recovered and opened using a procedure adapted from Orange County Water District (Don Phipps, personal communication). Towards the end of the testing period, elements were removed from the last pressure vessel and transported to Stanford for autopsy. Elements were disassembled within 24 hours after arrival and specimens were collected for organic content, relative fraction of carbohydrate and protein, ICP, XPS, and Auger analysis. Methods are detailed in an Appendix E. Selected elements were collected for laboratory cleaning tests.

6.4.2. Laboratory cleaning

Membrane coupons were taken from fouled membranes and placed in a flat-sheet cross-flow system. Acid and base cleaning steps were performed and performance was recorded before, in between and after cleaning. A fouled membrane element was also shipped to AMI for cleaning at their facilities. Cleaning was performed under pressure with a sequence of AM-11 and AM-22.

6.4.3. Geochemical Modeling

Equilibrium thermodynamic calculations were conducted in conjunction with laboratory testing to study the cause of RO membrane fouling. Mineral saturation states and phase diagrams for the aqueous speciation and solubility of $SiO_{2(aq)}$, HCO_3^-, Ca^{2+}, Mg^{2+} and Fe^{2+} were calculated with the Geochemist's Workbench (version 6.0) software package distributed by Rockware Earth Science Software, Golden, CO (Geochemist's Workbench® is a registered trademark of the University of Illinois). The thermodynamic calculations were conducted using the composition of the Gilroy RO concentrate. Because the separation process causes increased concentrations at the membrane surface (concentration polarization) precipitation will predominantly occur immediately adjacent to the RO membrane surface. To take this effect into account, the concentrations of Na^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, HCO_3^-, and SiO_2(aq) were evaluated at concentrations 10 times higher than the bulk feed solution. All calculations were based on the thermodynamic database supplied with the Geochemist's Workbench software package.

6.4.4. Fouling Experiments at Gilroy

After collecting normal operational data at the Gilroy site for 120 days, we studied system behavior under fouling conditions. The system was operated to allow execution of the fouling experiments. Membranes were removed from the system for autopsy on Day 150, 185, 206 and after the study was complete. In addition, we connected a flat-sheet test cell to the high-pressure brine flow concentrate line and exposed different membrane samples to brine flow under simulated treatment conditions. We measured flux in the flat-sheet cell and brought membrane swatches back to the laboratory for analysis. In addition, we allowed material to accumulate on the membrane surfaces for subsequent autopsy, and observed membrane performance under different treatment. These results are summarized below.

7. Project Outcomes

7.1. Gilroy Pilot Plant Evaluation

In the first period (10/17/06 - 2/06/07), the Gilroy RO unit reduced TDS levels from 770 mg /L in the feed to approximately 11 mg/L in the permeate, resulting in an average salt rejection of 98.4% (standard deviation (STD) ± 0.22%). During this period, the plant was operated at a recovery level of 83% (STD ± 1.6%).

7.1. 1. Startup and Operational Experiences

One RO unit was delivered to Gilroy from AMI in February 2006. Installation of electrical and piping infrastructure at SCRWA commenced in late April 2006, after an extended period of rainy weather. The following months were spent installing the ground water supply pump, resolving configuration problems, and installing sampling ports and the antiscalant pump and reservoir. Startup was on October 17, 2006 and the plant operation began without significant problems.

7.1.2. Gilroy Feed Water Quality

The feed water quality at the Gilroy site is indicated in Table 6 (Laboratory reports are given in Appendix F). Noteworthy details are the relatively high concentrations of calcium (84 mg/L) and magnesium (51 mg/L), and the presence of 40.2 mg/L silica. The

absence of nitrate and the presence of dissolved iron indicate anaerobic conditions. The TDS concentrations are above the EPA National Secondary Drinking Water Regulations (EPA, 2003) and within the 700 – 850 mg/L range that is often unfit for irrigation.

Table 6. Feedwater Quality at the Gilroy Site

Water quality characteristics	Units	Average[a]	Stdev	Stdev %
Calcium	mg/L	84.1	6.1	7
Iron	ug/L	523.3	48.1	9
Magnesium	mg/L	51.1	3.2	6
Silica	mg/L	40.2	2.5	6
Sodium	mg/L	129.0	17.7	7
Turbidity	NTU	0.8	0.7	92
Bicarbonate Alkalinity (as CaCO3)	mg/L	355.3	20.2	6
Carbonate Alkalinity (as CaCO3)	mg/L	0.0	0.0	
Hydroxide Alkalinity (as CaCO3)	mg/L	0.0	0.0	
Total Alkalinity (as $CaCO_3$)	mg/L	355.3	20.2	6
TDS[b]	mg/L	767.1	18.1	2
Chloride	mg/L	125.4	4.0	3
Nitrate	mg/L			
Sulfate	mg/L	132.3	5.7	4
Dissolved Organic Carbon	mg/L	2.1	0.1	6

Note:

a — Average of 12 measurements;

b — Reported as total filterable residue (at 180 ^{o}C).

7.1.3. Gilroy Trace Organics Wastewater Indicator Compounds Data

The results of the trace organics analyses are summarized in Table 7.

Pharmaceuticals and miscellaneous compounds were absent in the feed water with the exception of traces of alkylphenol ethoxylate metabolites, collectively called APEMs. The presence of these APEMs indicates that a fraction of the groundwater may originate from wastewater. Concentrations of these compounds are too low, however, to draw firm conclusions as to the origin of the water. All specific compounds were below the detection limit in the permeate, indicating efficient removal by RO, as expected.

Table 7: SCWRA Gilroy: Occurrence of Wastewater Indicator Compounds[a,b]

Analytes	Blank	Feed	Permeate
Pharmaceuticals (ng/L)			
Acetaminophen	n.d	n.d	n.d
Caffeine	n.d	n.d	n.d
Carbamazepine	n.d	n.d	n.d
Carisoprodol	n.d	n.d	n.d
Gemfibrozil	n.d	n.d	n.d
Ibuprofen	n.d	n.d	n.d
Iminostilbene[c]	18	37	n.d
Ketoprofen	n.d	n.d	n.d
Naproxen	n.d	n.d	n.d
Primidone	n.d	n.d	n.d
Propanolol	n.d	n.d	n.d
Hormones(ng/L)			
Estradiol	n.d	n.d	n.d
Estriol	n.d	n.d	n.d
Estrone	n.d	n.d	n.d
EE2	n.d	n.d	n.d
APEOs and APEMs (ng/L)			
Octylphenol	n.d	826	n.d
OP1EC	n.d	172	n.d
OP2EC	n.d	142	n.d
OP1EC	n.d	172	n.d
OP2EC	n.d	142	n.d
NP1EC	n.d	451	n.d
NP2EC	n.d	291	n.d
Others (ng/L)			
Bisphenol A	n.d	n.d	n.d
NBBS	n.d	n.d	n.d
Tris(2,3-dichloropropyl)phosphate	n.d	n.d	n.d
Tris(3-chloropropyl)phosphate	n.d	n.d	n.d
Oxadiazon	n.d	n.d	n.d

Note:

a — Reported values are averages of two samples for blanks, three samples for feed and permeate;
b — Reporting limit approximately 1 to 10 ng/L except for carisoprodol and ketoprofen, where it was approximately 70 ng/L;
c — Iminostilbene data is suspect because one blank was positive;
n.d — not detected.

7.1.4. Gilroy RO Unit Performance Evaluation

The initial operational set points at the Gilroy site were feed 17.9 GPM, concentrate 2.9 GPM, permeate 15.0 GPM and recycle flow 5.0 GPM, corresponding to a recovery of 79%. The anti-scaling agent was added at approximately 7 mg/L. For the first 120 days, data were collected manually and there were few interruptions. Thereafter, the system was modified for automated data collection.

Hydraulic performance: Figures 3 and 4 display the flow rates and the pressure data collected during the first three months of operation (10/17/06 - 2/06/07).

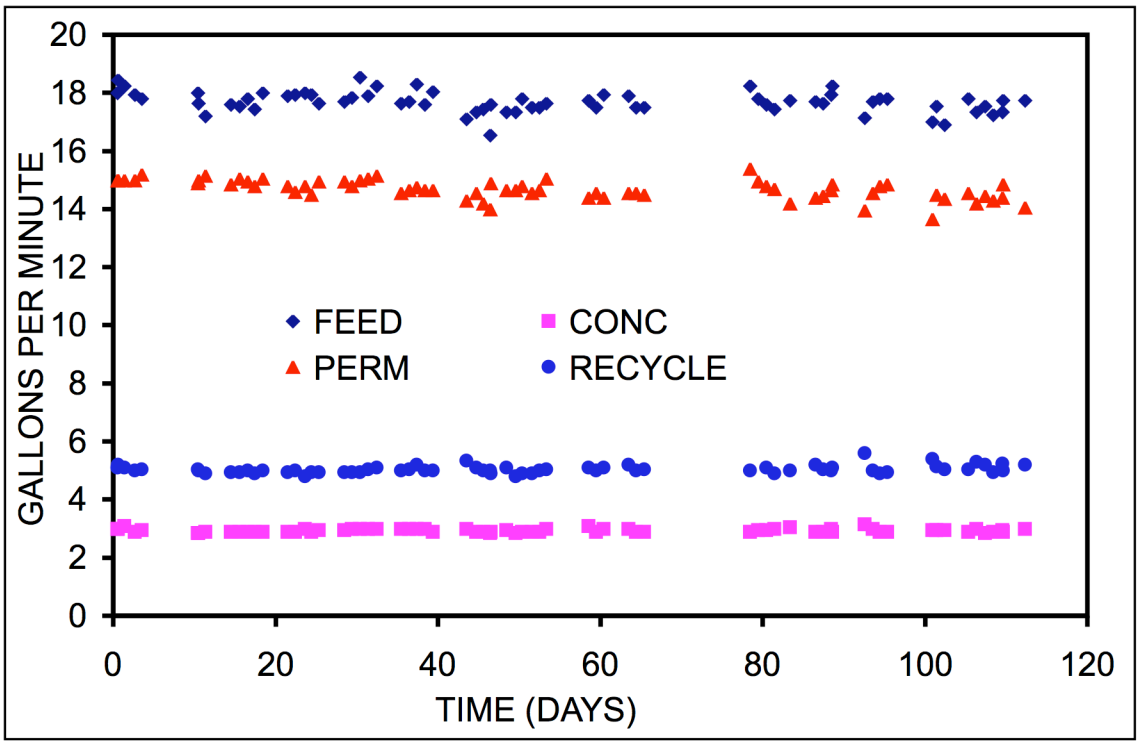


Figure 3. Gilroy plant: flows in feed, permeate, concentrate and recycle in the first period (10/17/06 - 2/06/07).

The flows during this time were maintained at the set points by manually adjusting pressure during site visits (often daily). The short data gaps were due to maintenance, the 13-day data gap was during the holiday break from December 22 through January 3.

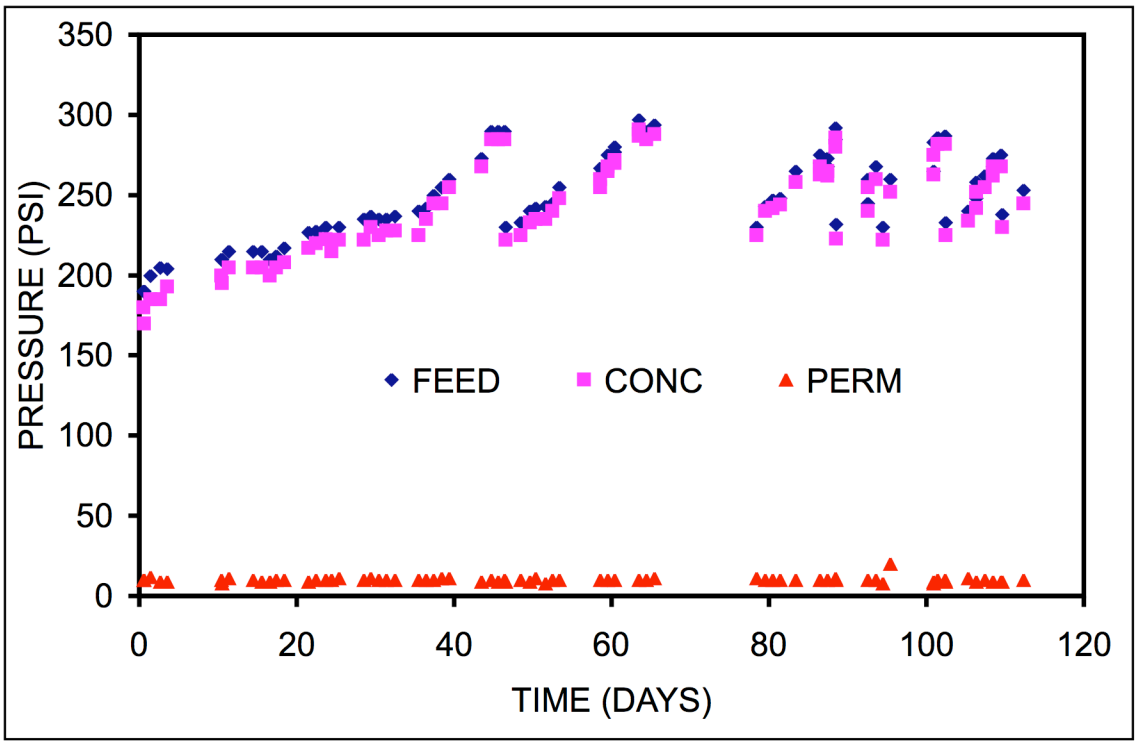


Figure 4. Gilroy plant: pressure profiles in the feed, concentrate and permeate during the initial period (10/17/06 - 2/06/07) while maintaining the flows shown in Figure 3.

The initial feed pressure increase (during the first 2 to 3 days of operation) to approximately 210 psi was attributed to membrane compaction. During the following four weeks, the pressure increased slowly by approximately 15% to 300 psi, which is the manufacturer's specified operational limit for these membranes. At this time, the system was cleaned with an acid solution (AM-11), after which water flux was restored and the operating pressure was reduced to about 225 psi. After another 2-week period, the feed pressure was again approaching 300 psi, at which point, the system was shut down for two weeks for winter break. Upon returning and restarting the system, the required feed pressure had dropped back to about 225 psi even though the system was not cleaned using a normal cleaning procedure suggesting either that the foulants (inorganic scale or biological deposits) redissolved.

Although the feed appeared free of hydrogen sulfide, hydrogen sulfide odor was noticed occasionally in the permeate flow. The presence of hydrogen sulfide is an indication for biological sulfate reduction, which may have been the caused by biological membrane fouling. Whether biological process was the cause for membrane fouling was studied during the subsequent fouling study discussed below.

From this point forward, cleaning was changed from AM-11 to 0.06% hydrogen peroxide assuming that sulfide was either a symptom or the cause for the observed fouling. The cleaning procedure used was simply flushing the system with 50 gallons of permeate water (3 times the system void volume), followed by the 50 gallons of 0.06% hydrogen peroxide solution, followed by 50 gallons of permeate water all at 2-3 gallons/minute.

This was found to be at least as effective as cleaning with AM-11, and at less than 10% the chemical cost. This solution is also non-hazardous and can be discarded into any waste stream.

The pressure difference between the feed and the concentrate ("delta pressure") averaged 7.5 psi and ranged from 2 and 10 psi (except during the startup phase where some values were higher). There was no significant upward trend over time, indicating that the accumulation of material within the high-pressure conduit was insignificant.

Salt Rejection and Water Quality: Figures 5 and 6 show the TDS data, and Figure 7 shows the pH data, and Figure 8 indicates the overall performance of the plant in terms of recovery and rejection.

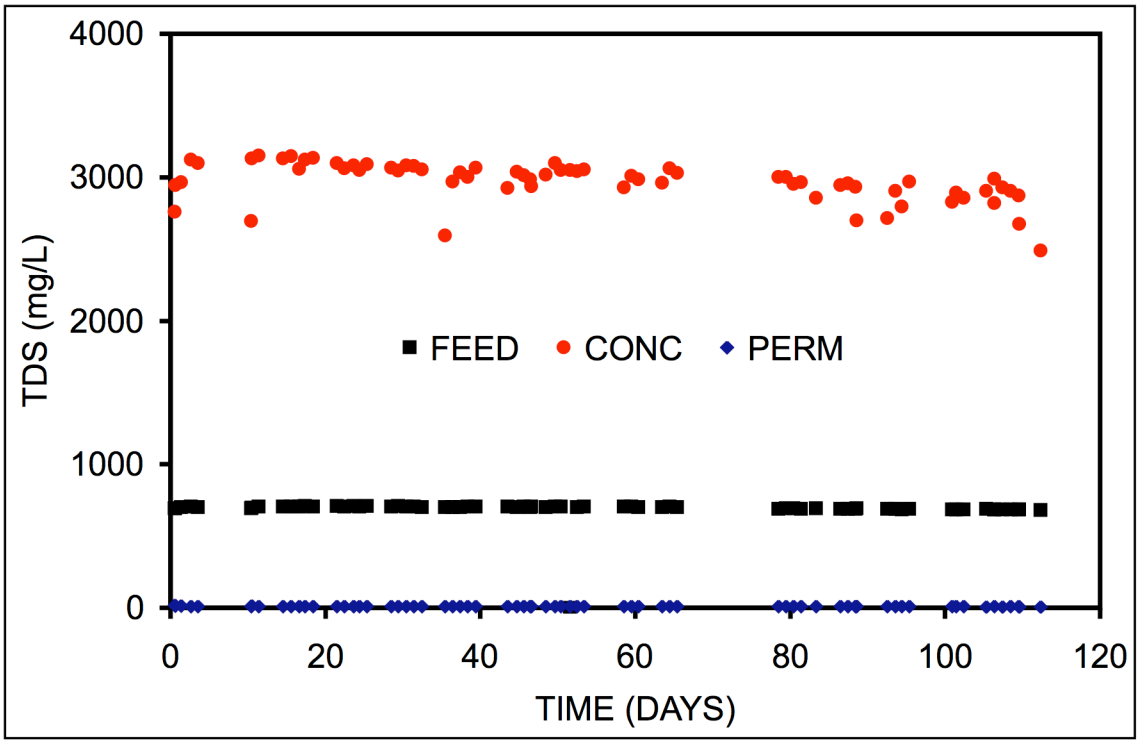


Figure 5. Gilroy plant: TDS concentration history in feed, concentrate and permeate (10/17/06 - 2/06/07).

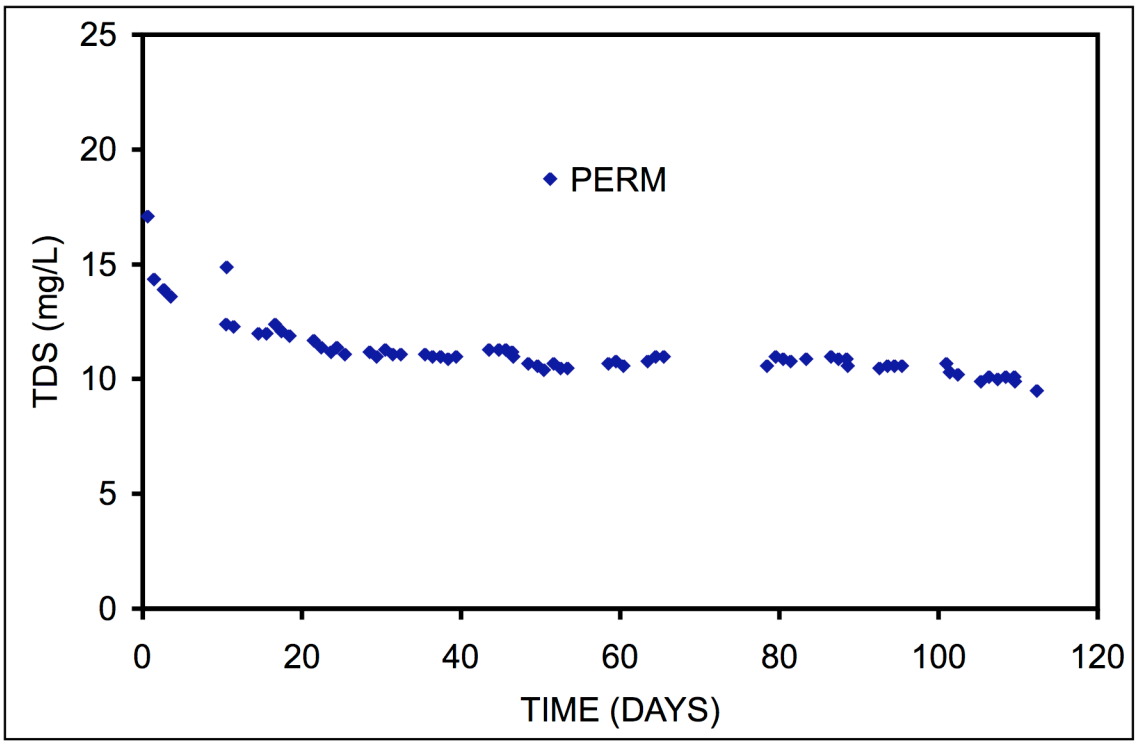


Figure 6. Gilroy plant: TDS in permeate concentration.

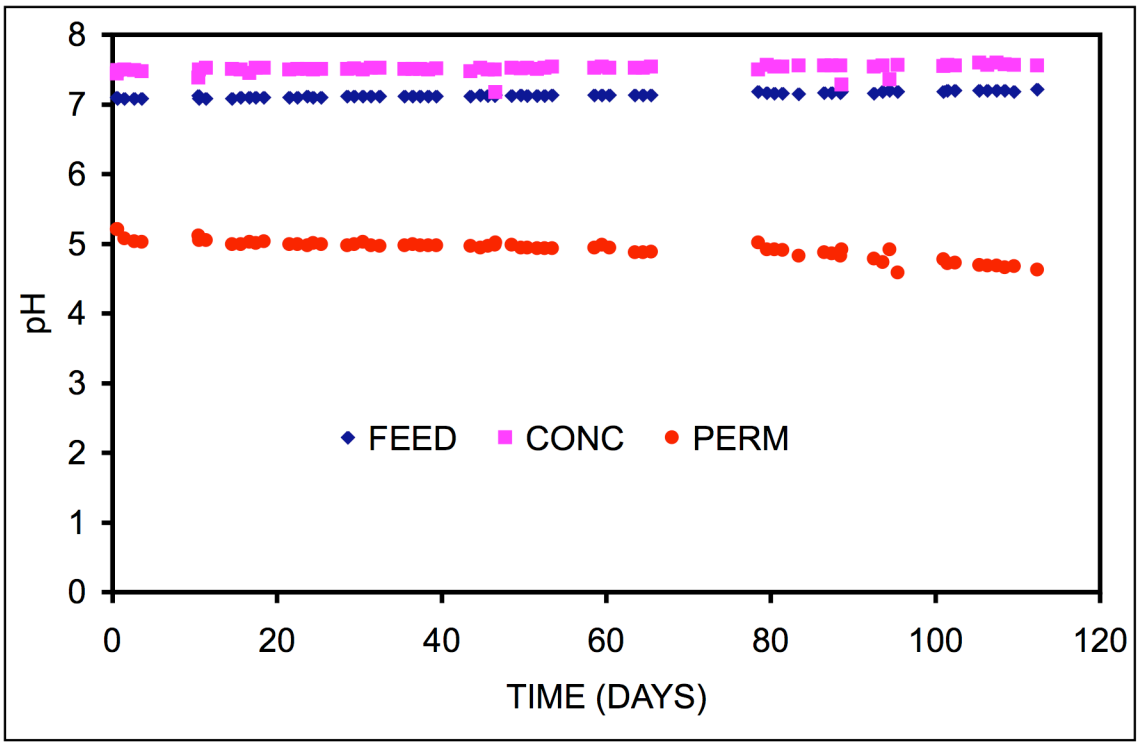


Figure 7. Gilroy plant: pH profiles.

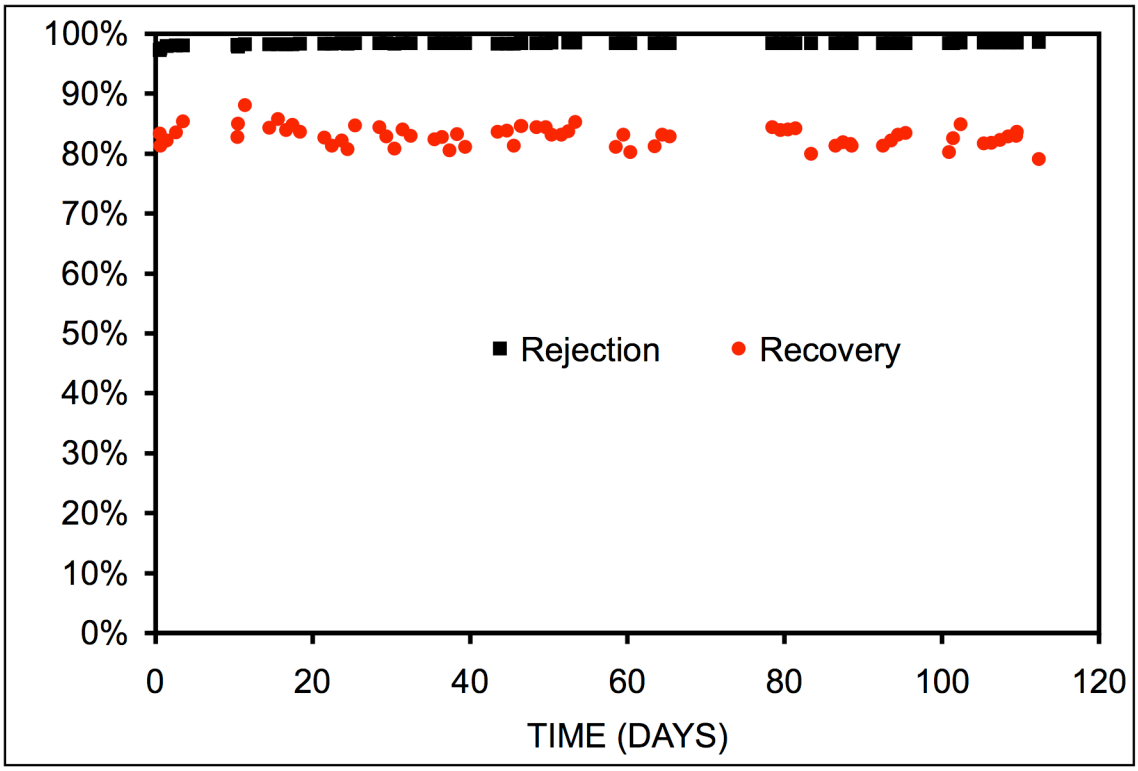


Figure 8. Gilroy plant: salt rejection and water recovery.

The TDS data shown in Figure 5 indicate that the TDS (measured as electroconductivity) in the feed and in the concentrate remained relatively constant. The permeate TDS, which is shown in greater detail in Figure 6, decreased during the compaction period and then remained relatively stable at approximately 11 mg/L. Apparently salt rejection was largely independent of flow resistance and fouling. The pH in the concentrate was stable and higher than in the feed (Figure 7). The permeate pH was lower than in the feed, as expected. This observation has been observed by Belkacem et al. and is explained by the fact that H^+ and CO_2 permeate more easily through negatively charged membranes than the negatively charged counter ions (Belkacem et al., 2007). The pH decreased during the first 2 to 3 days by about 0.2 pH units; during the remaining study period, the pH decreased by approximately half a pH unit. The decrease appeared more rapid after the 13 day down period (at the end of the year). A possible explanation is that the isoelectric point of the membrane was lowered at that time. Figure 8 indicates that the overall performance of the RO plant in terms of salt rejection and water recovery was relatively stable with the average salt rejection at 98.4% (standard deviation (STD) ± 0.22%) and the water recovery at 83% (STD ± 1.6%).

7.2. San Benito Pilot Plant Evaluation

The San Benito RO unit was operated at an average water recovery of 81% (STD ± 2%). Under these conditions, TDS levels were reduced from approximately 1227 mg /L in the feed to approximately 59 mg/L in the permeate, corresponding to an average salt rejection of 95% (STD ± 0.8%).

7.2.1. Startup and Operational Experiences

The field site in San Benito County was identified in March 2006 and site preparations began shortly thereafter (installation of electrical connections, piping, ground preparation, etc.). Acquisition of required permits was initiated at approximately that time. By end of August, installation of the site was nearly complete. A major unanticipated plant modification was installation of a pressure tank in-line with the well pump. System operations were started on October 13, 2006.

In the fall of 2006, the region experienced unusually harsh weather conditions with heavy storms in rapid succession followed by regional power failures. Unfortunately, the RO system was not protected against power failures. Sudden loss of power caused the precipitation a white solid and extensive fouling of the membranes, instrumentation and recycle feed line. These rainstorms also caused the soil in the vicinity of the site to soften, preventing vehicle access to the site. On October 18, 2006, a power failure shut down the system. The sudden loss of power stopped the flow with highly oversaturated brine remaining in the RO system. Salt precipitation caused fouling and operation was stopped. Cleaning was impossible until November 15 because the soil was too muddy to move in the cleaning unit.

The system was restarted on November 17. Four days later, another power failure caused the RO system to shut down again. Again, logistical problems and difficult site access delayed cleaning until January 2007. During the cleaning process, the recycle line, recycle valve, and the sensors were found to have significant scale deposits. To flush cleaning solutions through the recycle line, it was necessary to modify the system plumbing and install an additional cleaning outlet. In addition, protective features against sudden loss of power were installed and the software was modified to record historic data. After these modifications, we were able to begin collecting operating data on March 3, 2007. On March 12, another power failure shut the system down for nearly 24 hours but the plant modifications prevented damage from occurring. Over the next three days, the flow meters were calibrated and retested (Days 10-12). Again, with the exception of the recycle flow meter, the calibrations were within 5%. The manufactures settings for the recycle flow meters were set for a 2-inch pipe instead of a ½-inch pipe and therefore significantly incorrect and probably contributed to the scaling when system power was disrupted previously. On March 17, the software was modified to extend the TDS probe scale to handle recording historic data at higher TDS concentrations (change from 5000 to 8000 ppm max) and a wiring problem was fixed. Scaling of the concentrate TDS probe was found to be a regularly occurring problem requiring short shut down periods in order to acid clean the probe. On Day 34, the concentrate flow meter was found to be scaled and non-responsive. Over the next 10 days, we had problems with scaling and power failures. After an AM-11 acid cleaning on Day 48, the system operated stably.

7.2.2. San Benito Feedwater Quality

The feed water quality at the San Benito site is indicated in Table 8. Concentrations of calcium (101.4 mg/L) and magnesium (106.8 mg/L) were relatively high (somewhat higher than at Gilroy). Silica was present at 32.6 mg/L and was a potential scalant. Nitrate was absent but in contrast to Gilroy, dissolved iron was absent, indicating a somewhat higher geochemical reducing potential in the groundwater than at Gilroy. The

TDS concentrations are above the EPA National Secondary Drinking Water Regulation limits (EPA, 2003) and preclude agricultural use.

Table 8. Feedwater Quality at the San Benito Site

Parameters	Units	Average[a]	STDEV	Rel. Stdev
Calcium	mg/L	101.4	7.9	8
Iron	ug/L			
Magnesium	mg/L	106.8	9.5	9
Silica	mg/L	32.6	3.0	9
Sodium	mg/L	312.3	35.1	11
Turbidity	NTU	6.7	11.6	175
Bicarbonate Alkalinity (as CaCO3)	mg/L	578.0	9.5	2
Carbonate Alkalinity (as CaCO3)	mg/L	0.0	0.0	
Hydroxide Alkalinity (as CaCO3)	mg/L	0.0	0.0	
Total Alkalinity (as $CaCO_3$)	mg/L	578.0	9.5	2
TDS[b]	mg/L	1393	20.6	1
Chloride	mg/L	281.3	8.8	3
Nitrate	mg/L			
Sulfate	mg/L	249.0	3.6	1
Dissolved Organic Carbon	mg/L	2.4	0.1	5

Note:

a — Average of 12 measurements;

b — Reported as total filterable residue (at 180 ^{o}C).

7.2.3. San Benito Trace Organics Wastewater Indicator Compound Data

Table 9 indicates the occurrences of wastewater indicator compounds in blanks, feed and permeate in a sample taken on March 29, 2007.

As at Gilroy, pharmaceuticals were absent with the exception of traces iminostilbene. o,o'-Iminostilbene (5H-dibenz[b,f]azepine) a tricyclic secondary amine used as an anticonvulsant. However, this compound was also detected in one blank. In addition, traces of APEMs, NBBS, and tris(3-chloropropyl)phosphate were detected. Taken together, these results indicate that a fraction of the groundwater may originate from wastewater but this hypothesis needs to be confirmed. In the permeate only a trace of tris(3-chloropropyl)phosphate was detected indicating these compounds are removed, although not to 100%.

Table 9: San Benito: Occurrence of Wastewater Indicator Compounds[a,b]

Analytes	Blank	Feed	Permeate
Pharmaceuticals (ng/L)			
Acetaminophen	n.d	n.d	n.d
Caffeine	n.d	n.d	n.d
Carbamazepine	n.d	n.d	n.d
Carisoprodol	n.d	n.d	n.d
Gemfibrozil	n.d	n.d	n.d
Ibuprofen	n.d	n.d	n.d
Iminostilbene	n.d	26	n.d
Ketoprofen	n.d	n.d	n.d
Naproxen	n.d	n.d	n.d
Primidone	n.d	n.d	n.d
Propanolol	n.d	n.d	n.d
Temazepam D5 (surrogate std)	n.d	n.d	n.d
Hormones (ng/L)			
Estradiol	n.d	n.d	n.d
Estriol	n.d	n.d	n.d
Estrone	n.d	n.d	n.d
EE2	n.d	n.d	n.d
APEOs and APEMs (ng/L)			
Octylphenol	n.d	n.d	n.d
Nonylphenol	n.d	n.q	n.d
OP1EC	n.d	n.d	n.d
OP2EC	n.d	n.d	n.d
NP1EC	n.d	341	n.d
NP2EC	n.d	967	n.d
Others (ng/L)			
Bisphenol A	n.d	n.d	n.d
NBBS	n.d	10	n.d
Tris(2,3-dichloropropyl)phosphate	n.d	n.d	n.d
Tris(3-chloropropyl)phosphate	n.d	21	5
Oxadiazon	n.d	n.d	n.d

Note:

a — Reported values are averages of two samples for blanks, three samples for feed and permeate;
b — Reporting limit: approximately 1 to 10 ng/L except for carisoprodol and ketoprofen, where it was approximately 70 ng/L;
n.d. — not detected;
n.q. — detected as a trace but not quantified.

7.2.4. San Benito RO Unit Performance Evaluation

Hydraulic performance: Figures 9 and 10 display the flow rates and the pressure data collected.

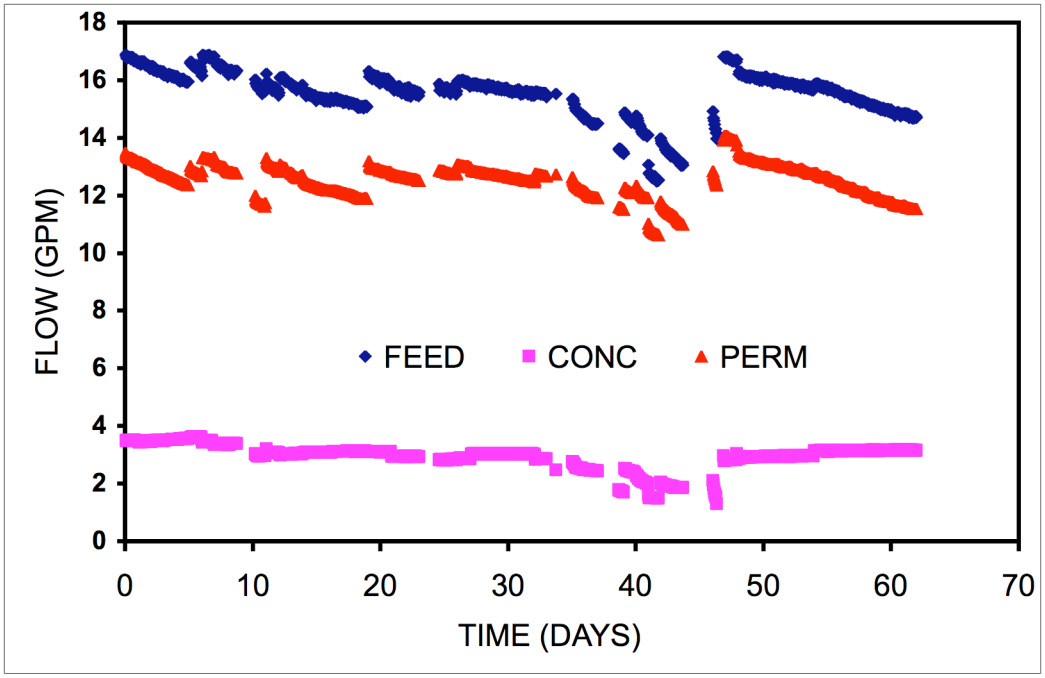


Figure 9. San Benito: Flows in the feed, concentrate, and permeate.

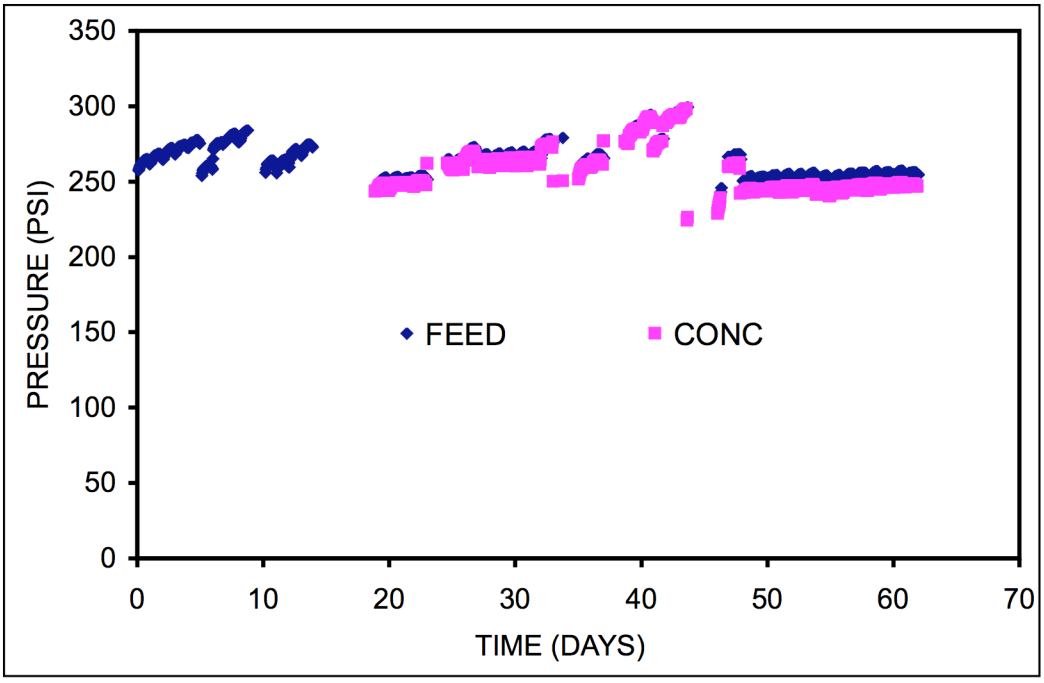


Figure 10. San Benito: Pressure profiles in the feed, concentrate and permeate during the initial period.

At startup on March 3, automated data collection began. The initial operational set points were feed 17 GPM, concentrate 3.5 GPM, permeate: 13.5 GPM and recycle flow 5.3 GPM, corresponding to a recovery of 79%. This was about 10% lower than during the initial operations in the fall in order to decrease initial system pressure. The initial pressure was approximately 260 psi and increased to approximately 280 psi within 5 days, after which the system received a 0.06% peroxide cleaning, followed two days later by a AM-11 (acid) cleaning.

The operating pressure following the acid cleaning decreased back to approximately 260 psi. Two days later, another power failure shut the system down for nearly 24 hours.

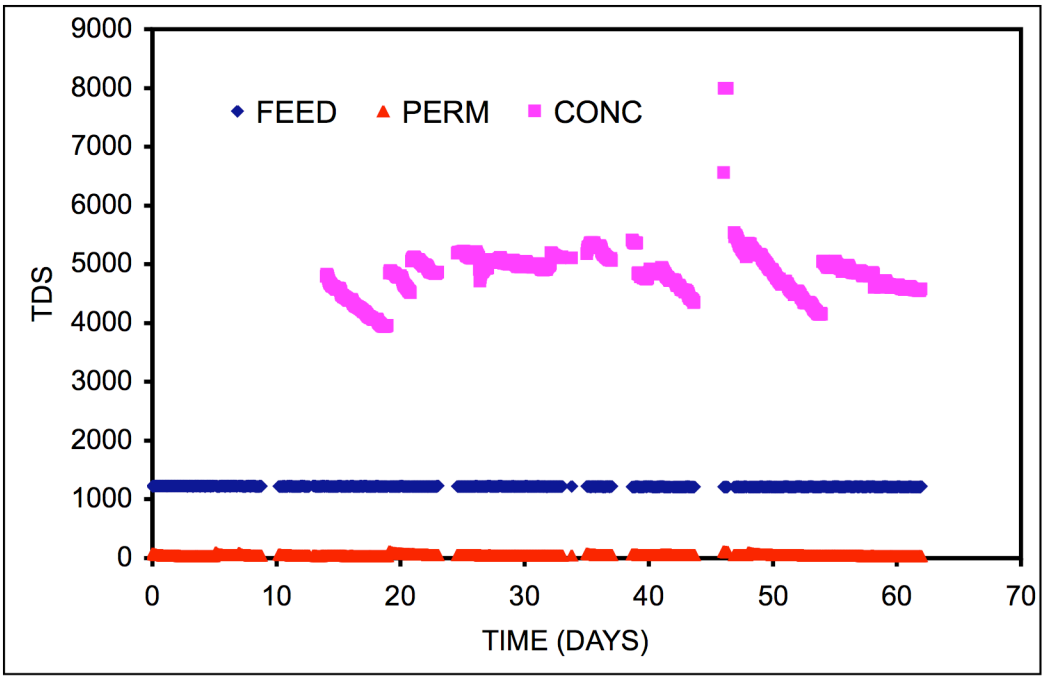


Figure 11. San Benito: TDS concentration history in feed, concentrate and permeate.

Salt Rejection and Water Quality: The results of scaling on the concentrate TDS probe and its cleaning can be seen in Figure 11. The TDS data indicate the TDS (measured as electroconductivity) in the feed remained relatively constant. Electroconductivity measurements are sensitive to the ion composition and thus are not linear. The TDS concentration in the permeate flow decreased rapidly after cleanings before approaching a value of approximately 60 mg/L, as shown in Figure 12. The reason for this dependence was not investigated, but may be caused by the antiscalant AM-11 used to clean the membranes. The reasons for the decreasing TDS after cleaning events are not clear.

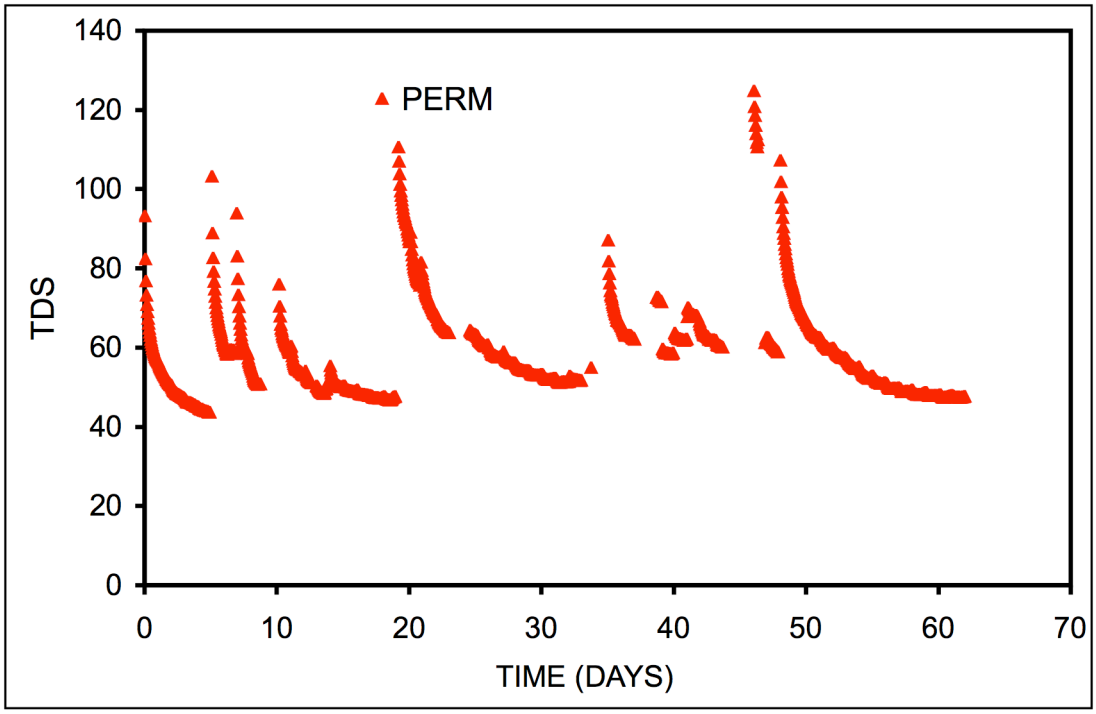


Figure 12. San Benito: TDS concentration in permeate.

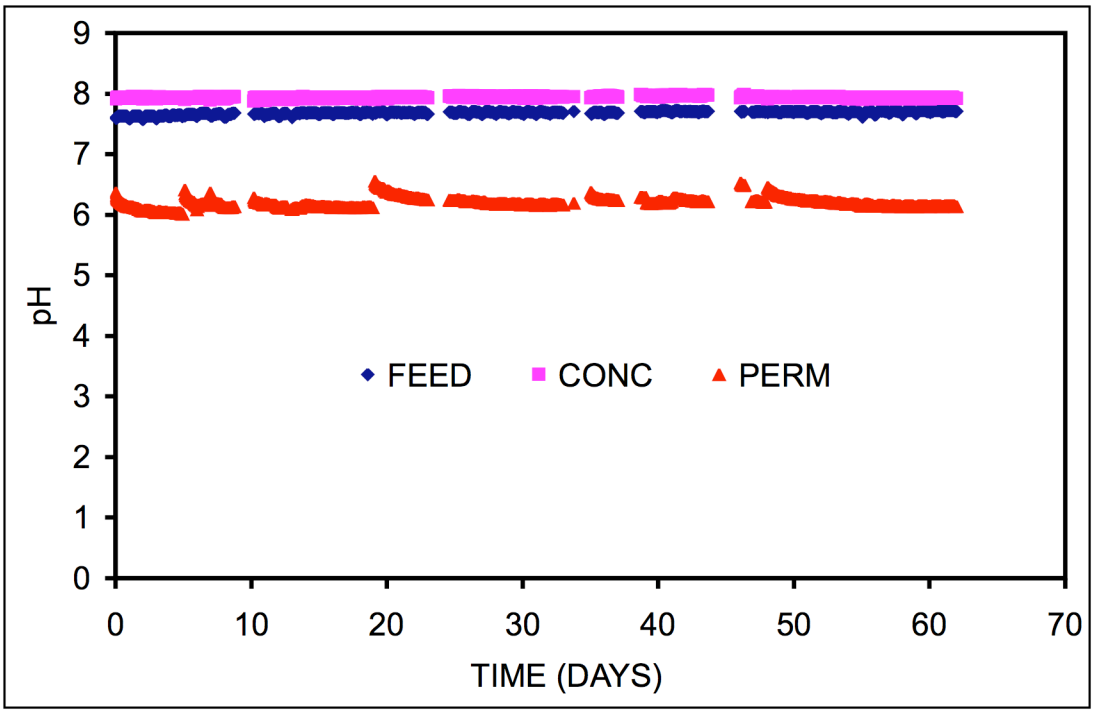


Figure 13. San Benito plant: pH profiles.

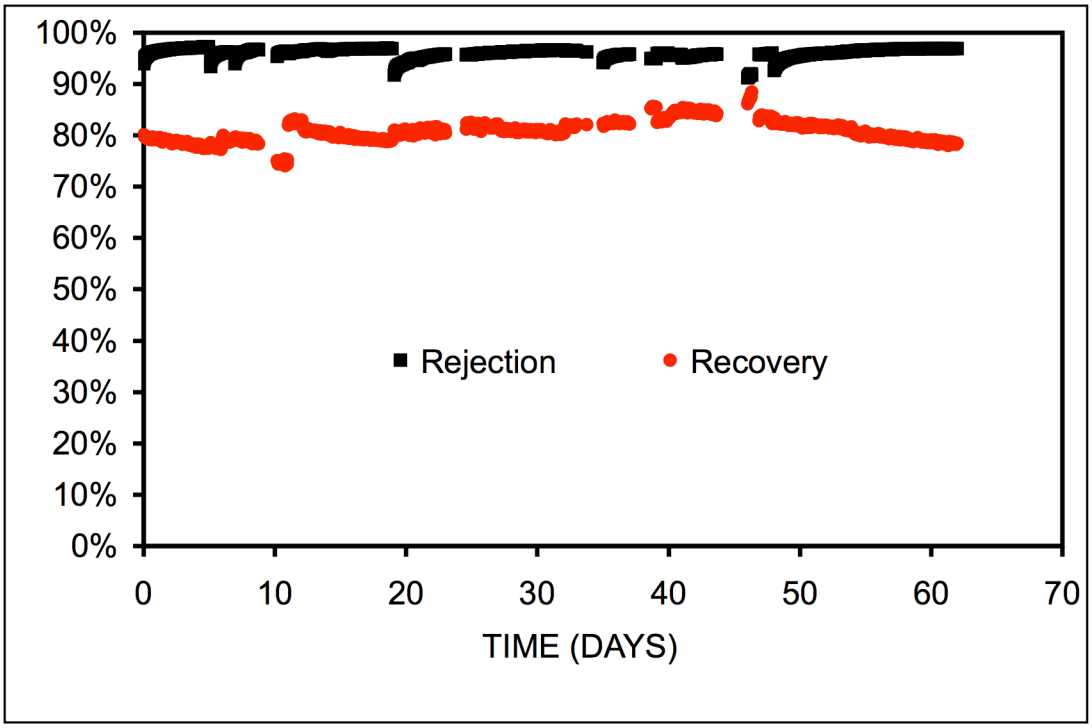


Figure 14. San Benito: Salt rejection and water recovery.

The spikes in pH coincided with cleaning events and the conductivity spikes. The cause of this is unclear at this point. Figure 14 shows the performance of the RO unit at San Benito. Average salt rejection and water recovery at this plant for was 96% (STD ± 0.29) at a water recovery of 79% (STD ± 3.1).

7.3. Membrane Fouling and Autopsy Studies

7.3.1. On-site Fouling Studies

RO membranes tend to become fouled by scaling salts, inorganic oxides, colloidal material, or biological matter. This process occurs under "normal operating conditions" but depends heavily on the type of feedwater that is treated. Fouling involves the entrapment of materials in the feed/brine path or is caused by localized deposition directly on the membrane surface. The fact that the pressure along the feed channel (feed inlet to concentrate outlet), the "delta pressure", did not increase indicated that fouling was a membrane surface phenomena. As detailed below, the amount of material collected from the membrane surface was relatively small. As part of the membrane autopsy investigation, material deposits were collected from Gilroy and San Benito membranes at the end of the test period and investigated as described below.

Figures 15 and 16 show the hydraulic performance and Figures 17 and 18 indicate TDS removals during the fouling study.

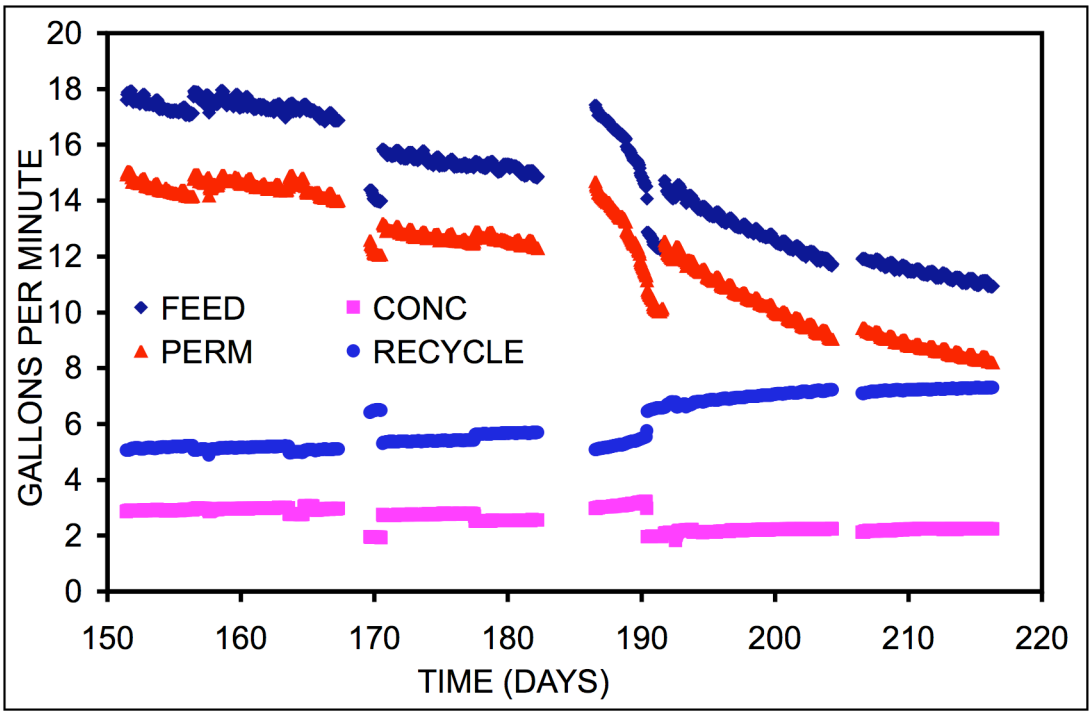


Figure 15. Gilroy: feed, permeate, recycle and permeate flows during the fouling study period. Changes in operational conditions are indicated in Figure 16.

At the beginning of the fouling studies, a single flat cell was installed and the addition of antiscalant (Flocon 260) was terminated. After about 15 days (on Day 165), 50 gallon 0.06% hydrogen peroxide cleaning was performed which had little impact. At Day 169, the system was cleaned with 120 gallon hydrogen peroxide (0.06%) and flowrates were decreased intentionally upon startup and the single flat cell was changed to a three flat cell configuration. At Day 183, the system was acid cleaned after pulling the last membranes from pressure vessels 3 and 4. A new antiscalant pumping system was installed to add Flocon 260 at a lower dosage, about 3.5 mg/L. Flowrates were increased upon startup. Five days later, the system was cleaned three times, peroxide followed by acid followed by peroxide. Then the system was restarted at a lower flowrate. Flowrates were allowed to decrease over the next 28 days. Elements were removed for internal autopsy at Day 206 and for autopsy by AMI on Day 218.

During the first 35 days of the fouling studies, the antiscalant (Flocon 260) was not added. When the pressure built up, a 0.06% hydrogen peroxide cleaning was performed but this had no impact. Upon restarting, flows were decreased in order to lower operating pressures.

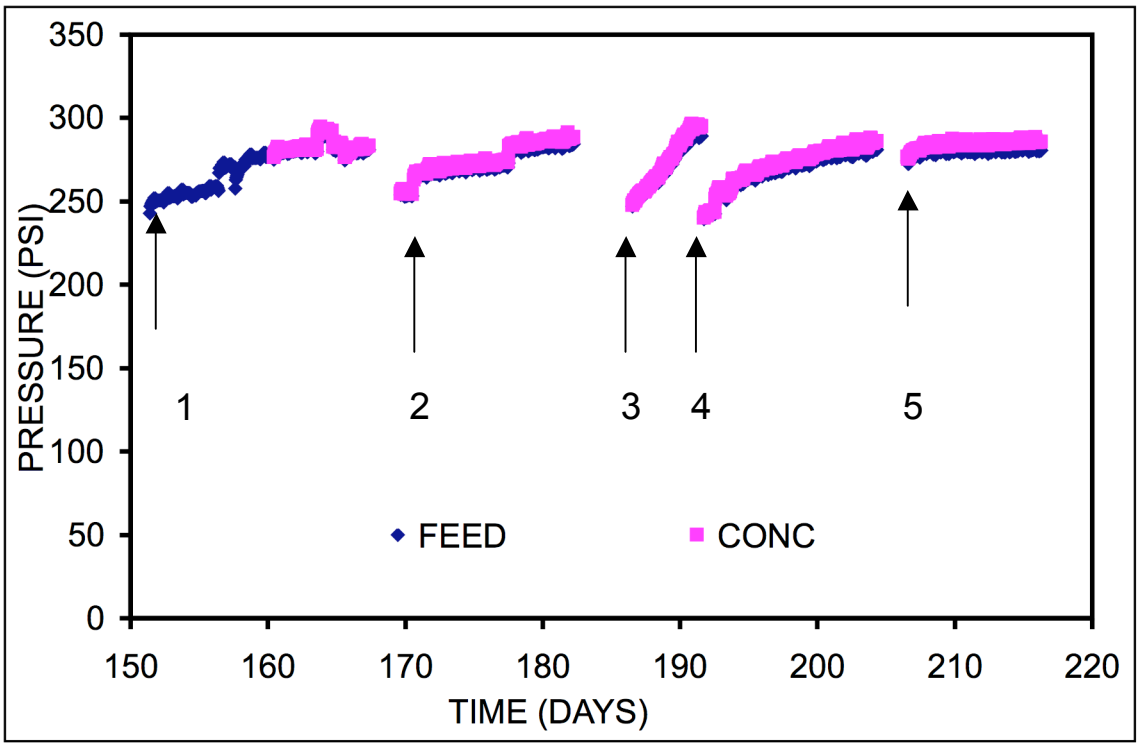


Figure 16. Gilroy: feed, concentrate and permeate pressures during the fouling study period. 1: Hydrogen Peroxide, Restart at Lower Flows Cleaning; 2: Acid (AM-11) Cleaning; 3: Start Low Dose Falcon 260; 4:Hydrogen Peroxide/Acid/Hydrogen Peroxide Cleaning; 5: Removal of membrane for autopsy.

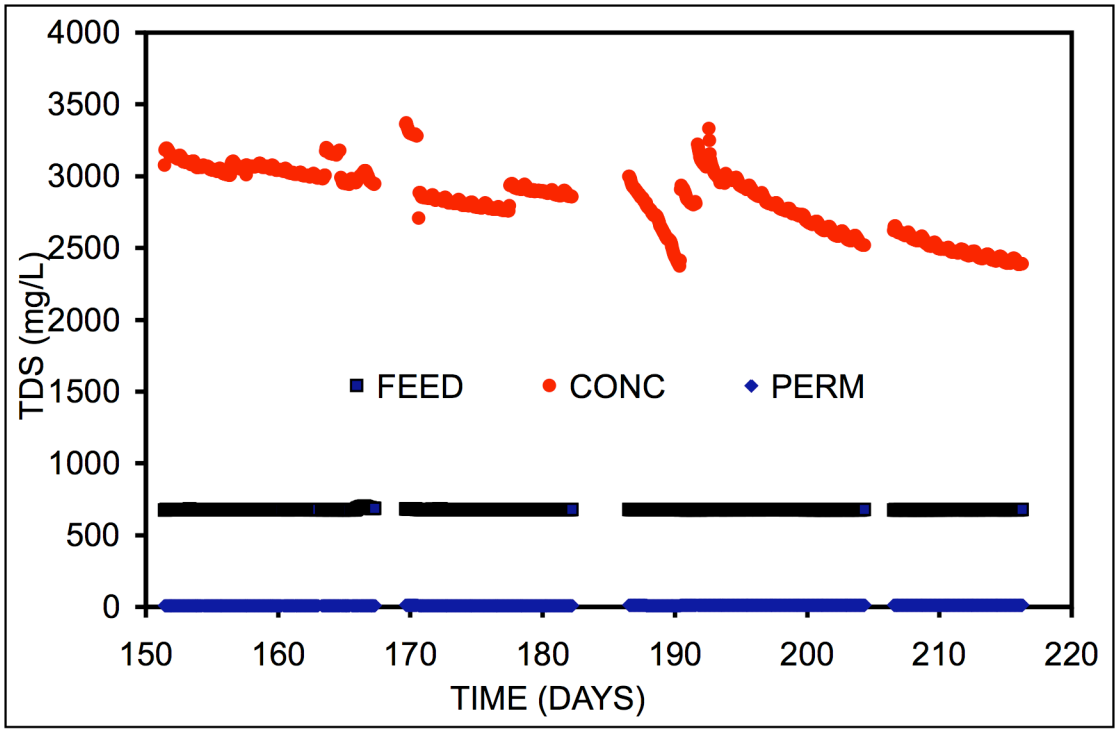


Figure 17. Gilroy: TDS in feed, concentrate and permeate flows during the fouling study period.

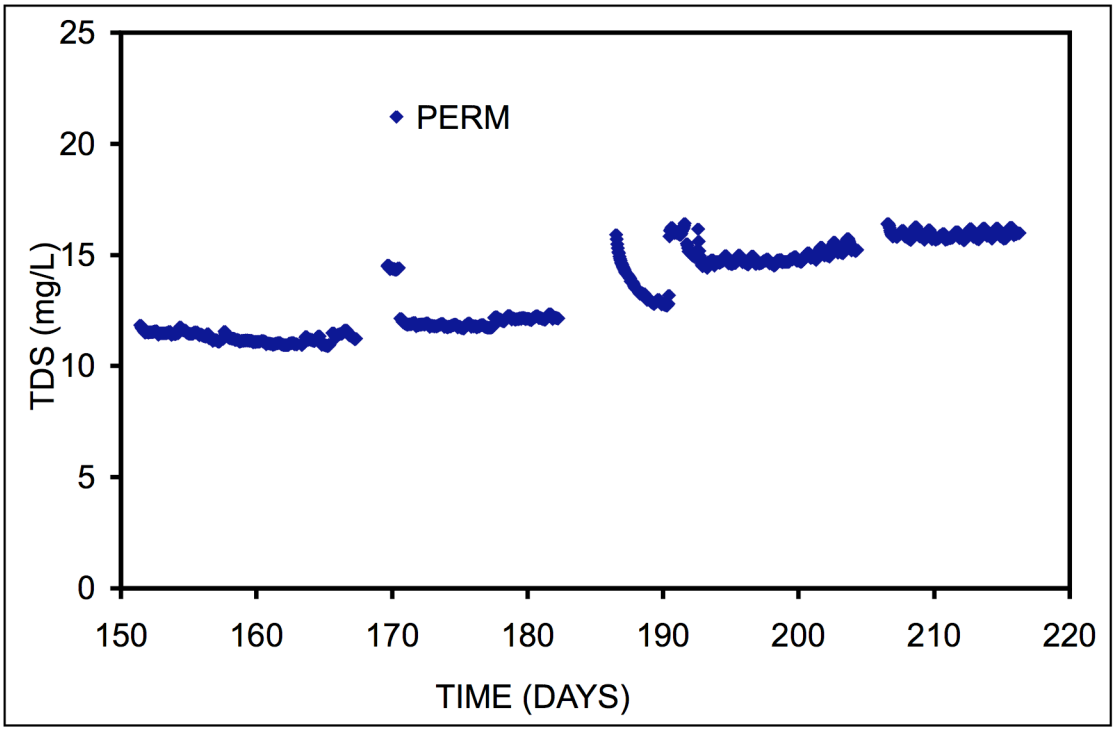


Figure 18. Gilroy: TDS in permeate during the fouling study period.

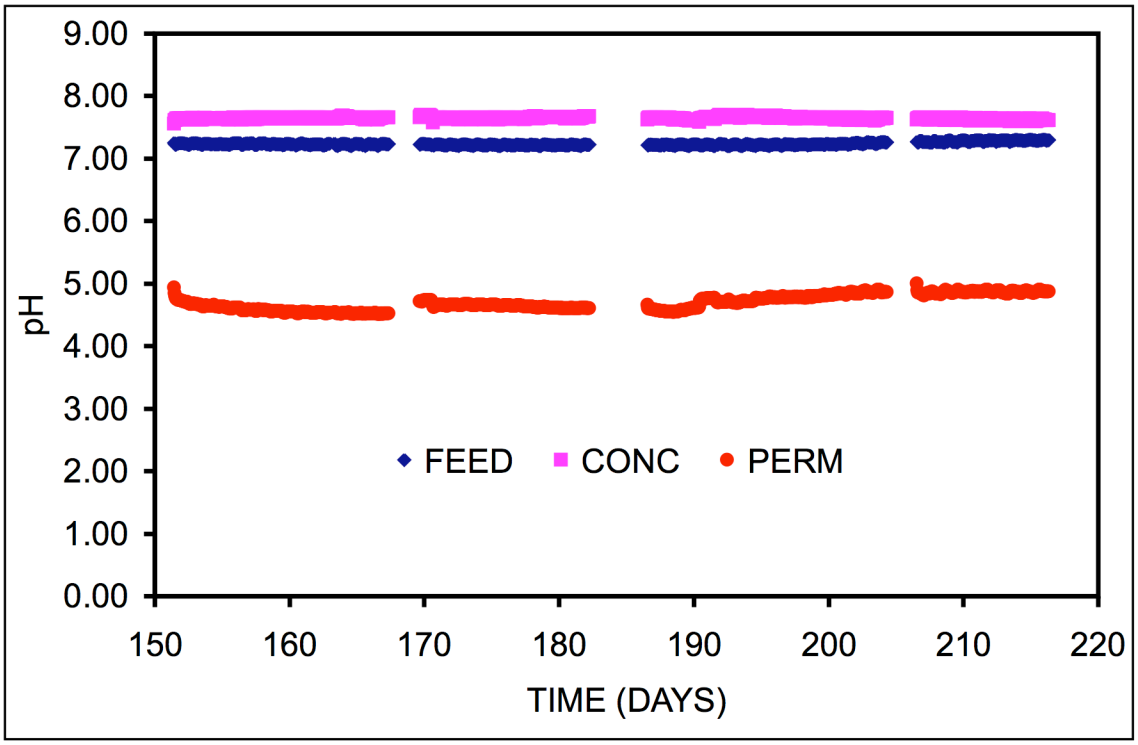


Figure 19. Gilroy: pH during the fouling study period in the feed, concentrate, and permeate.

The variations in concentrate TDS show that it is sensitive to variations in concentrate flow for relatively fixed feed and permeate flows (Figure 17). As shown in Figure 18, the permeate TDS shows a gradual decrease in salt rejection over the time period of these fouling studies. Of interest is the data around Day 190 where there is a decrease in TDS over a period of time after restarting the system. This was commonly seen in the San Benito RO system and may indicate a leakage, possibly from extracting and replacing membranes for autopsy. The pH data shown in Figure 19 show the expected pH shifts.

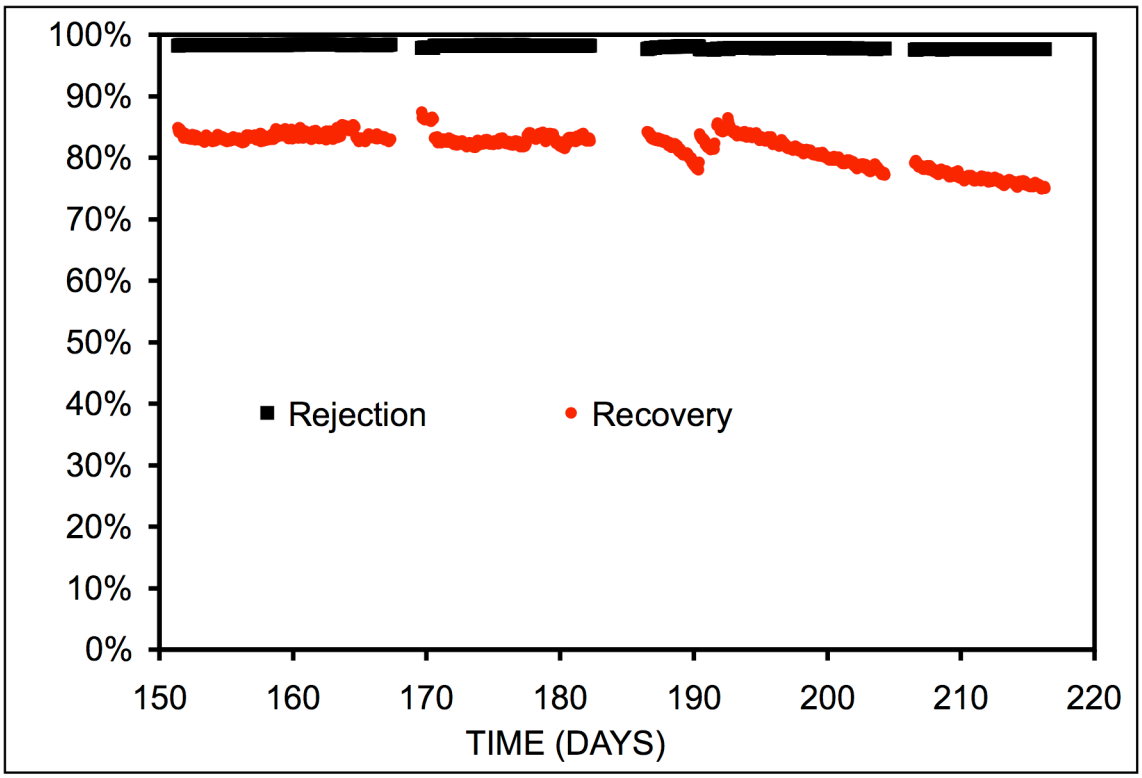


Figure 20. Gilroy: rejection and recovery during the fouling study period.

Figure 20 indicates rejection and recovery during the fouling study period when cleaning was discontinued. Recovery declined from Day 190 onward after the last cleaning event.

7.3.2. Laboratory Cleaning Tests of Fouled Membranes

At the end of the testing period, we studied the effect of membrane cleaning in the laboratory under controlled conditions using flat sheet cells. Elements were disassembled by cutting off the end-pieces, unrolling the sheets, and removing the spacer. Section of the fouled membranes (swatches) were mounted in flat sheet test cells, and tested before and after cleaning. For testing the San Benito swatches, we used solutions of 1,200 mg/L and 3,000 mg/L sodium chloride in deionized water. Table10 summarizes the results for both sites. Results are shown in Table 11.

Table 10. Summary of Laboratory Cleaning Tests

	Gilroy	San Benito
Laboratory Flat sheet	3000 ppm NaCl, 200 psi and 1.6 L/min cross flow, flat sheet. Cleaning with AM11 then AM22. Flux increase 57%	1200 ppm NaCl, 200 psi and 1.6 L/min cross flow, flat sheet. Cleaning with AM 124 then AM 22. Flux increase 15%.

AMI first applied AM-22, which was followed by AM-11. They noticed flux improvement by 43% to 1310 gpd, which is about half of the specified flux of a virgin membrane. Salt rejection was at 98.7%, near the specified level.

Table 11. Laboratory Cleaning Tests of Membranes Fouled On-Site at Gilroy

Manufacturer Specifications		Before Cleaning		After AM 22 cleaning		After AM-11 cleaning (final)	
Flow	Rejection	Flow	Rejection	Flow	Rejection	Flow	Rejection
2800	98.0%	917	97.8%	1080	98.6%	1310	98.7%
100%		33%		39%		47%	

7.3.3. Analysis of material deposited on membrane surface

7.3.3.1. Sampling and visual inspection

Field and laboratory cleaning tests showed a fraction of flux loss was resistant to cleaning. To gain insight into the fouling mechanism an attempt was made to characterize the fouling material. Terminal elements of both plants were brought back to the laboratory and subjected to autopsy using a number of chemical and spectroscopic methods. Upon opening, the elements and the fouling layer were visually inspected. Photographs in Figure 21 depict the material collection and samples of the dried material.

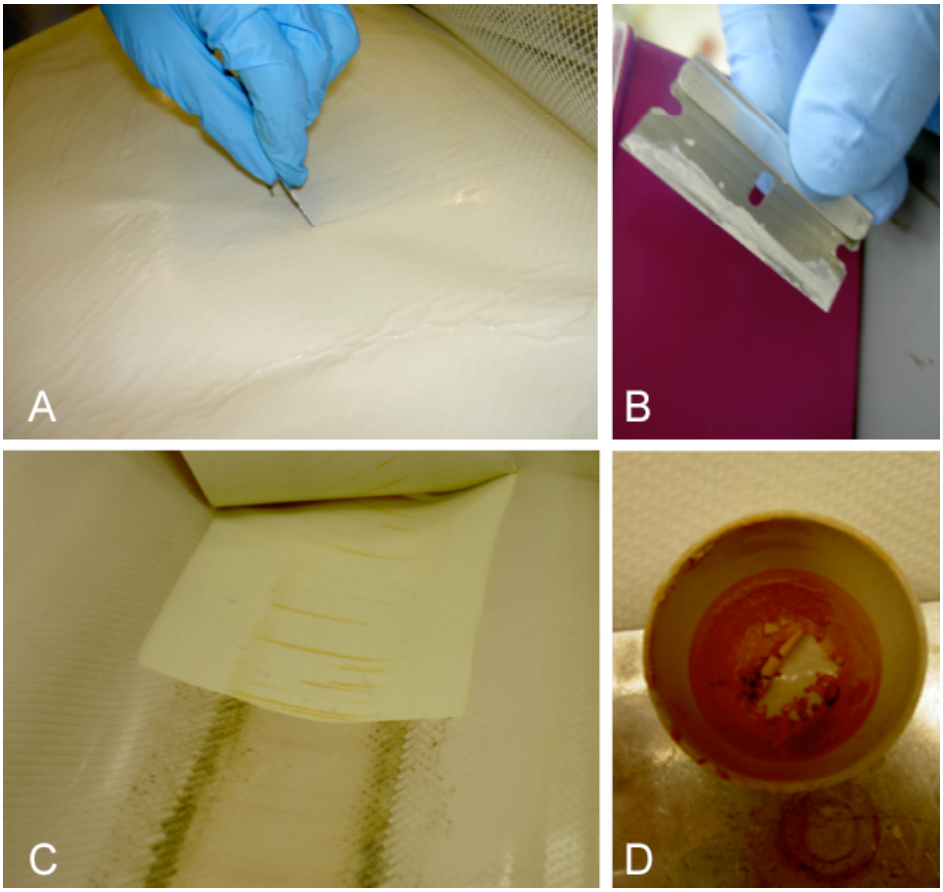


Figure 21. Visual inspection of membrane and collection of fouling material.

(A) Gilroy – Deposit collection using a sterile razor blade. (B) Gilroy – fouling material collected on a razor blade. (C) San Benito – The fouling material is the brown-green

material deposited on the permeate spacer. (D) San Benito – The collected fouling material appears orange.

7.3.3.2. Evaluation of biological fouling

The collected material was analyzed for aggregate organic content, total carbohydrate and protein using methods indicated in Appendix E. Results shown in Table 12 for total organic carbon indicate an organic content percentage for Gilroy of 8.8% (STD ± 1.3%) and for San Benito of 27.1% (STD±4.3%).

Table 12. Organic Contents in Cake Materials Collected on Fouled Membranes

Protein and carbohydrate values were below the quantitation limits and are therefore not reported. The biomass content (protein and carbohydrate) was relatively low suggesting

Sample	Surface Area sampled (cm^2)	Dry Mass (mg/cm^2)	Inorganic Mass (mg/cm^2)	Organic Mass (mg/cm^2)	Organic Fraction %	Inorganic Fraction %
Gilroy						
Gilroy 1	2442	0.331	0.303	0.028	8.4	91.6
Gilroy 2	6006	0.169	0.152	0.017	10.2	89.8
Gilroy 4	3736	0.185	0.171	0.014	7.4	92.4
Average					**8.8**	**91.2**
STD					**1.3**	**1.31**
San Benito						
San Benito 1	4392	0.019	0.014	0.005	25.83	74.17
San Benito 2	1601	0.067	0.046	0.021	31.91	68.09
San Benito 3	1656	0.044	0.033	0.010	23.58	76.42
Average					**27.10**	**72.90**
STD					**4.31**	**4.31**

that fouling in these elements could have been caused by inorganic deposits. Inorganic deposits (scales and silica) are expected to be the dominant fouling factor at the end of a RO train where the brine concentration is highest (Huiting et al. 2001).

Biological activity might have contributed to flux loss in the first elements of the RO train but more detailed studies are required to evaluate this hypothesis. Operational experiences and circumstantial evidence suggest that microbial activity may have been a contributing factor (directly or indirectly) to fouling: smell of sulfide in permeate water (not in feed water) suggested microbial activity in the RO train, the flux is restored by long-term shut down and treatment with very dilute hydrogen peroxide restored flux. A possible fouling mechanism is the bioreduction of sulfate to sulfide and subsequent formation and deposition of insoluble iron sulfide.

7.3.3.4 Elemental Analysis of Deposited Materials Using Spectroscopic Methods

Analysis of the San Benito Cartridge Prefilter

A spent 5-micron prefilter from the San Benito plant was analyzed to identify solids that were retained from the well water. Figure 22 shows a picture of the filter taken from the San Benito and the Gilroy sites on after approximately 500,000 and 1,000,000 gal of use.

The two filters reflect the different geochemistry at the site, which was more reducing at the San Benito site. Samples of the discolored San Benito filter material were soaked in 0.2 mol/L nitric acid for several hours. The leachate was then diluted and analyzed with ICP. The results of these analyses are shown in Table 13. The data indicate the presence of iron but the form in which it was present cannot be determined. It appears likely that iron was present in soluble or colloidal form and was entrapped by the filter. The sulfide odor that developed after the deposits were dissolved in nitric acid may have been indicative for the presence of iron sulfides. Calcium and magnesium were also present at significant levels on the prefilter, and they probably existed in the forms of carbonate salts. Manganese was not found at significant level on the prefilter, which is consistent with the results shown in Figure 23.

Figure 22. Photograph of 5 micro pre-filters from San Benito (left) and Gilroy (right) sites after approximately 500,000 and 1,000,000 gal of use.

Table 13. ICP results for San Benito prefilter

Metal	Content, mg/g filter
Ca	4.5
Fe	22.9
Mg	3.4
Na	17.3

Analysis of the Gilroy and San Benito RO Membranes

Small coupons were cut from the spent RO membranes from the Gilroy and the San Benito plants and were leached in 0.2 mol/L nitric acid for several hours. The elements detected by ICP analysis are indicated in Figure 22. The metal contents were higher on the membrane from Gilroy, which had been in operation for 6 months compared to 3 months for membranes at San Benito. Of the elements detected, calcium and iron were present in the highest quantities, followed by magnesium and manganese, traces of barium, nickel and strontium. After the November 21 power failure at San Benito, a white precipitate was collected in the recycle loop and the feed channel and was analyzed using X-ray diffraction (XRD). The spectrum of this material (not shown) indicated mixtures of amorphous solid. Elemental and spectroscopic analyses didn't reveal the type of phases that were deposited on the membranes and causing the observed flux decline.

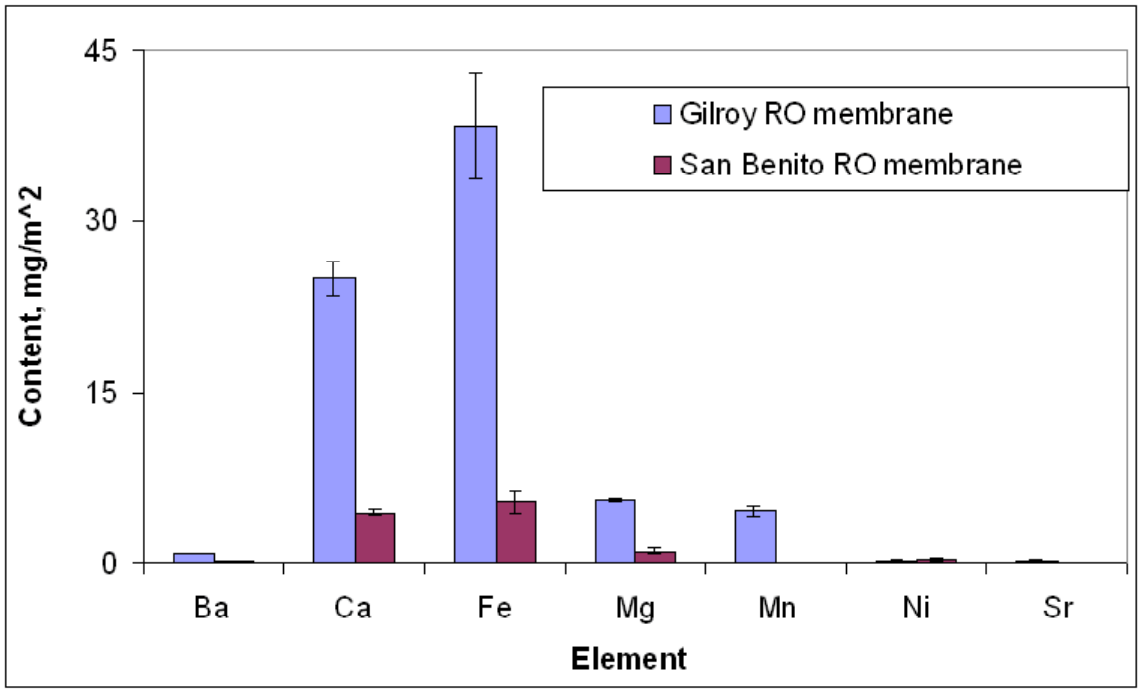
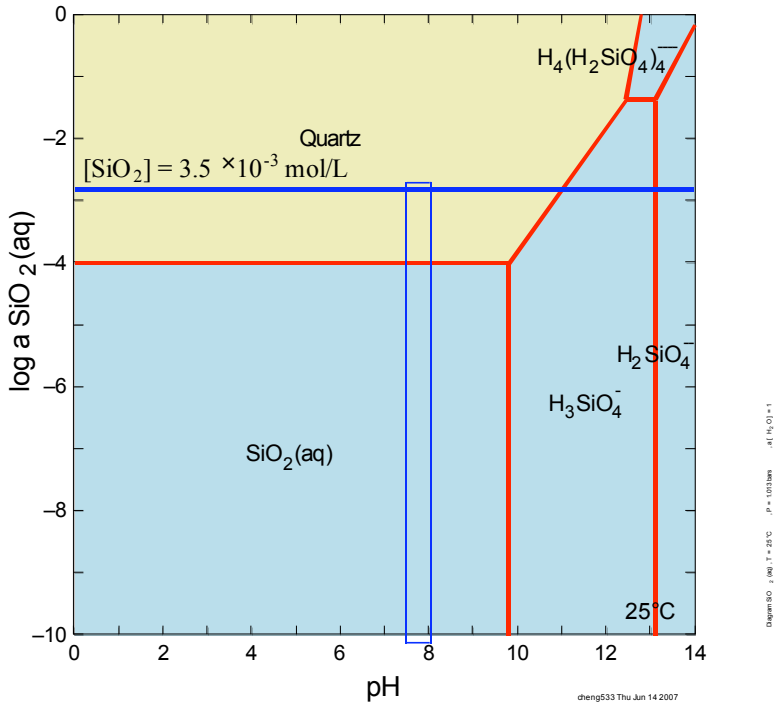


Figure 23. ICP analyses of deposited material collected from the Gilroy and San Benito sites. Error bars represent the standard deviation of 4-fold replicate analyses.

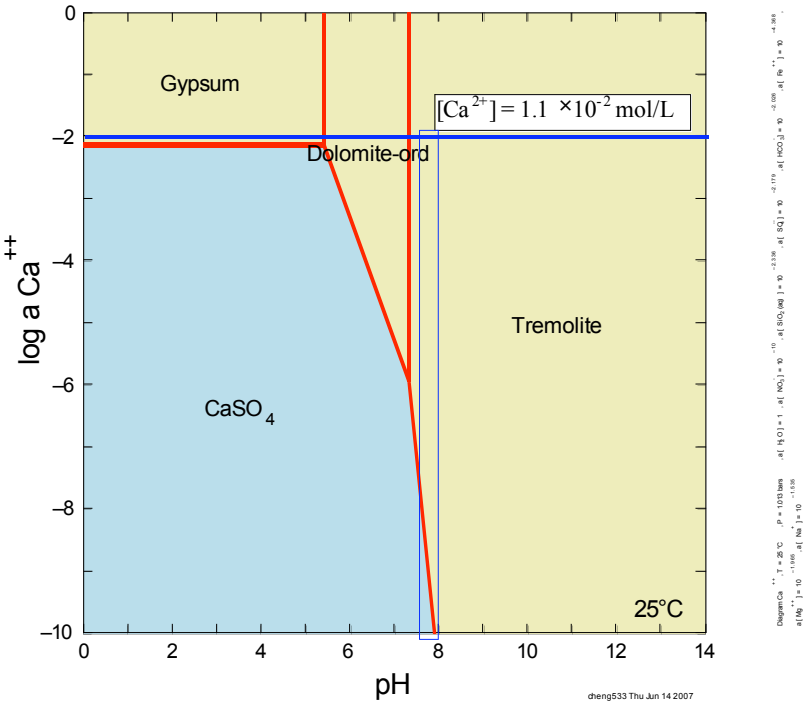
7.3.3.5. Supporting Geochemical Modeling Studies

Equilibrium thermodynamic calculations were conducted in conjunction with laboratory testing to study the cause of RO membrane fouling. Mineral phase diagrams for the aqueous speciation and solubility of $SiO_{2(aq)}$, Ca^{2+}, Mg^{2+} and Fe^{2+} were calculated with the Geochemist's Workbench (version 6.0) software package. Figures 24a to 24d show the phase diagrams for speciation of SiO_2, Ca^{2+}, Mg^{2+}, and Fe^{2+} in the RO concentrate of the Gilroy plant. At near neutral pH range, $SiO_{2(aq)}$ concentrations higher than 10^{-4} mol/L become supersaturated (Figure 24a). $SiO_{2(aq)}$ concentration in the RO concentrate (3.5×10^{-3} mol/L) is clearly above this limit, even without considering the concentration polarization effect. Amorphous silica does not appear on the phase diagrams here because it is not the thermodynamically stable form of SiO_2. The phase diagrams of Ca^{2+} (Figure 24b) and Mg^{2+} (Figure 24c) both suggest that dolomite controls aqueous solubilities of Ca^{2+} and Mg^{2+} at near neutral pH and that dolomite precipitation can occur in the RO concentrate even in the absence of concentration polarization effects. Finally, the phase diagrams of Fe^{2+} (Figure 24d) suggest that the Fe^{2+} (4.3×10^{-5} mol/L) is supersaturated in the RO concentrate with respect to minnesotaite in the pH range of 7.5-8.0. It should be noted that the concentration polarization effect further increases the precipitation of minerals in the concentration polarization layer near the RO membrane surface compared to that in the bulk solution. Modeling RO rejection and scaling using the ROSA software package indicated potential silica scaling (Appendix G.)

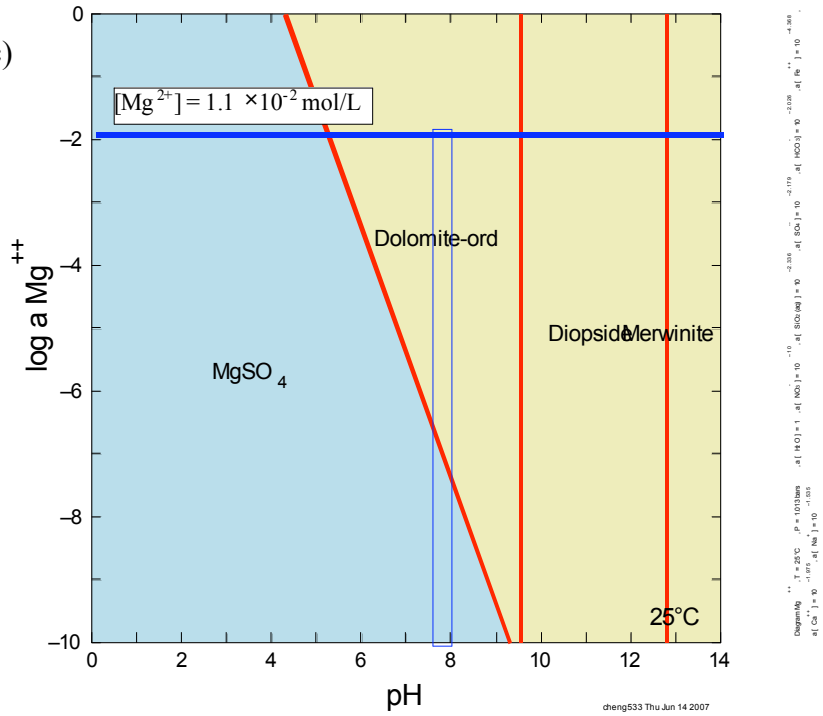
(a)


Quartz
[SiO2] = 3.5 ×10-3 mol/L
H4(H2SiO4)4--
H2SiO4-
H3SiO4-
SiO2(aq)
25°C
log a SiO2(aq)
pH
cheng533 Thu Jun 14 2007

(b)


Gypsum
[Ca2+] = 1.1 ×10-2 mol/L
Dolomite-ord
Tremolite
CaSO4
25°C
log a Ca++
pH
cheng533 Thu Jun 14 2007

(c)



(d)

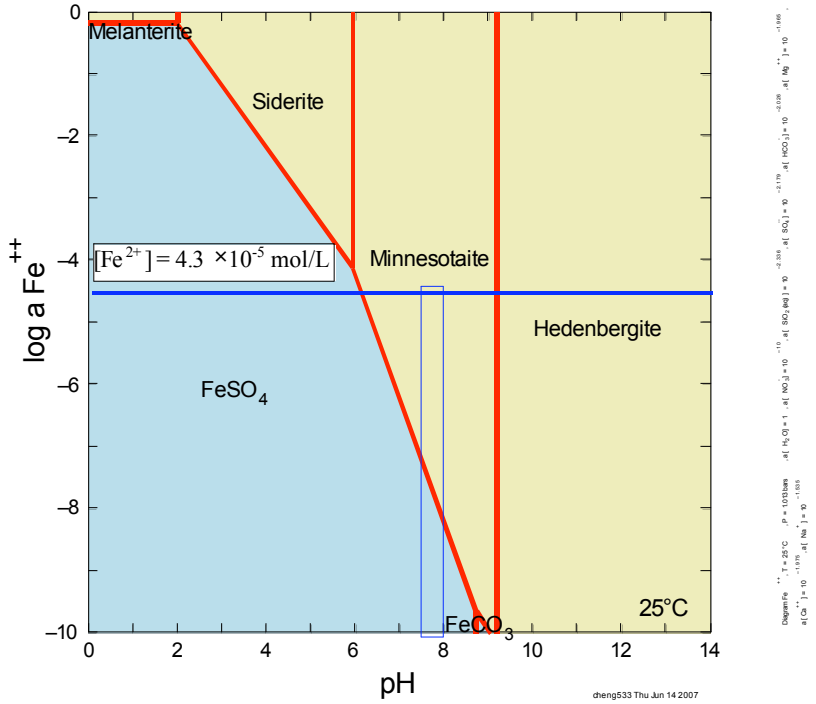


Figure 24. Stability diagram and the concentration of (a) silica, (b) Ca^{2+}, (c) Mg^{2+}, and (d) Fe^{2+} in RO concentrate of Gilroy plant. The pH of RO concentration is in the range of 7.5 to 8.0, as indicated in the diagrams.

Overall, the thermodynamic calculations indicate that significant silica precipitation can occur in the RO concentrate, while the precipitation and calcium-, magnesium-, and iron-

containing salts are also possible. These results are consistent with the high contents of calcium, magnesium, and iron in the prefilter and RO membranes observed in elemental analysis (with the exception of silicon, which was not measured). Confirmation of the chemical compositions of the fouling materials and the mineral phases that formed on the RO membranes was beyond the scope of this study. It will require more detailed laboratory and field investigations. Because the identity of the fouling materials remains unknown, the optimal antiscaling agents and cleaning procedures cannot be determined. Since manufacturers do not disclose the composition of the antiscaling agents, collaboration with manufacturers will be required to optimize the process.
These calculations are based on the assumption that the solid phases formed are thermodynamically controlled and do not consider the rate at which the precipitates are formed. Furthermore, the calculations consider only the crystalline phase while amorphous mineral phases almost always precipitate first. The modeling considers a closed system without accounting for the possible carbon dioxide passage through the membrane. Solid phases formed on the concentrate side of the membrane are not necessarily the cause for the observed flux decline because interactions with the membrane could depend on size, surface properties, and membrane-solid interactions, which are unknown. Because analytical data are consistent with the phases predicted by modeling, scaling inhibitors should be targeted towards to control the precipitation of silica, dolomite and potentially iron sulfide.

8. Economic Considerations

8.1. Implications of the RMC Study

RO desalination of groundwater in the San Juan Basin is constrained by the capacity of the groundwater basin to sustainably produce water (RMC, 2007). RMCs costs estimation for full scale RO groundwater demineralization considers extraction, storage and conveyance, demineralization, pre- and post-treatment, brine management and salt disposal. From modeling studies, RMC concluded that in the long-term withdrawals from the basin should not substantially exceed 4,300 AFY, which is the estimated maximum sustainable extraction capacity. The recommended design called for treating 2,641 AFY groundwater with a TDS of 1,800 mg/L and blending with groundwater to produce 3,000 AFY fresh water containing no more than 300 mg/L TDS. This scheme requires treatment of 541 AFY RO concentrate with a TDS concentration of 10,105 mg/L and is based on a water recovery of 83%.

Water recovery is one of the most important parameters in designing the demineralization system. Assuming water recoveries ranging from 75% to 98%, production of 3,000 AFY requires pumping of as much as 4,000 AFY or as little 3,061 AFY, respectively. One reason to maximize water recovery during desalinization process is to maximize the total volume produced while staying within the sustainable extraction limit. Two additional reasons for maximizing water recovery are: higher recovery rates lower the capital costs when normalized with respect to the production capacity, and, costs associated with brine management and disposal decrease with decreasing brine volume. The recommended treatment scheme is based on 83%, which is equal or close to the water recoveries maintained in this study, which were 83% at Gilroy and 81% at San Benito pilot. The 1,800 mg/L TDS value assumed by RMC is higher than the TDS values observed at

Gilroy and San Benito, which were on 770 mg/L and 1,227 mg/L, respectively.

8.2. Cost analysis of Groundwater desalinization at Gilroy and San Benito

The cost analysis provided below is based on the costs for the 3,000 AFY system recommended by RMC (2007). Key design parameters and specifications relevant to extrapolate cost calculations to San Benito and Gilroy conditions are summarized in Table 14.

Table 14. Partial list of assumptions for RMC cost estimate for desalination process and comparison with Gilroy and San Benito operational data.

Characteristic	RMC	Gilroy	San Benito
Groundwater TDS feed mg/L	1,800	770	1,227
Permeate TDS mg/L	97	11	59
TDS Removal	94.5%	98.4	95.0
Membrane System Water Recovery %	83	83	81
Chemical cleaning period	3 months (for 75% recovery)	bi-weekly	weekly

As indicated in Table 14, the water recoveries maintained at the pilot systems agree with the recovery of the recommended system (83%). However, the pilot systems were operated at sites with lower TDS concentrations. The permeate TDS concentrations were lower than the 1,800 mg/L assumed in the RMC study in both cases with essentially the same (San Benito) or slightly better percent TDS removals. The estimated chemical cleaning period for the conceptual system is 3 months at a water recovery of 75%, but was bi-weekly and weekly at Gilroy and San Benito, respectively. At the Gilroy site with a TDS of 700 mg/L, steady operation required less frequent cleaning (bi-weekly) than at San Benito, where the feed TDS was 1,227 mg/L and weekly cleaning was required. To extrapolate from these data to groundwaters with 1,800 mg/L is difficult. Desalinating 1,800 mg/L TDS groundwater at 75% water recovery may be possible with three-months cleaning intervals, increasing water recovery to 83% would almost certainly require much more frequent cleaning and higher anti-scaling additions.

The more severe scaling expected from desalinating 1,800 mg/L TDS groundwater leads to increased O&M costs (power, chemical, labor, and consumables) but should have little impact on capital costs of the desalination process. The impact of increased maintenance costs on the annualized unit costs calculated for a base case constructed from RMC data (XLE-4040 membrane and 3000 AFY production of 300 mg/L TDS water) is indicated in Table 15 for 10%, 20%, and 40% increases in the annual O&M costs assuming that other costs will remain the same. The financial assumptions are 30 years facility life and 5% interest rate.

Table 15. Impact of increases in O&M costs on annualized unit costs for increases of 10%, 20%, and 40% assuming constant capital costs, 30 years of facility life, 5% interest rate and 3,000 AFY production capacity.

Cost category	Base case[a]	+ 10%	+ 20%	+ 40%
Total Capital Cost	$28,610,000	$28,610,000	$28,610,000	$28,610,000
Consumables	$386,000	$424,600	$463,200	$540,400.0
Power	$392,000	$431,200	$470,400	$548,800
Labor	$94,000	$103,400	$112,800	$131,600.0
Chemicals	$54,000	$59,400	$64,800	$75,600.0
Annual O&M Cost	$926,000	$1,018,600	$1,111,000	$1,296,400.0
Present Worth O&M	$14,220,000	$15,660,000	$17,080,000	19,930,000
Total Facility Present Worth Cost	$42,830,000	$44,270,000	$45,690,000	$48,540,000
Annualized unit cost	$2,786,152	$2,879,827	$2,972,200	$3,157,596
Annualized Unit Cost ($/AF)	$929	$960	$991	$1,053
Annualized Unit Cost ($/hundred cubic feet)	$2.13	$2.20	$2.27	$2.42

a: Base case constructed from RMC's present worth cost analysis (system equipped with XLE-4040 membranes).

The cost analysis indicates that the relatively high capital costs diminish the impact on the annualized unit costs. To operate the system at sites with lower TDS would lower the O&M costs of the base case (assumed to be 1,800 mg/L TDS) and might lower the brine disposal costs. To evaluate the impact of increased O&M costs on the overall treatment costs considering the entire system, including groundwater extraction and conveyance, desalination treatment, concentrate management and product water storage and distribution, requires a more detailed analysis.

9. Conclusions, Lessons Learned, and Recommendations

9.1. Conclusions

Two pilot systems were designed, built, deployed, and operated at two different brackish groundwater sites, Gilroy and San Benito, both located in southern Santa Clara County. The results can serve as a starting point for a comprehensive evaluation of the potential of desalinating brackish groundwater as means to extend the local water supply. Specific conclusions are:

1. In terms of trace organic constituents, the groundwater at both sites showed no or minimal wastewater impact.
2. It was possible to desalinate brackish groundwater at both field sites to potable TDS standards using reverse osmosis.
3. Site-specific pilot evaluations are necessary even for sites situated relatively close to each other in the same groundwater basin. The differences in the quality of the

groundwater at Gilroy and San Benito were significant and as a result the two RO systems required different operating conditions.

4. Biological and inorganic fouling appear to have played a role at Gilroy but the individual contributions of these processes to the observed flux decline cannot be quantified. The fact that hydrogen peroxide reduced fouling at Gilroy suggests that microbial processes might have played a role.
5. Scaling was more difficult to control at the San Benito site, where the TDS levels were higher. San Benito autopsy data show the accumulation of iron on the prefilter and membranes, which might have played a role in scaling. Feedwater quality data did not indicate the presence of iron, however, suggesting that trace levels of iron (below the detection limit) might have significant impact over a long period of time.
6. Maintaining approximately 83% water recovery at Gilroy and San Benito required bi-weekly and weekly membrane cleaning. At sites with substantially higher TDS concentrations that those at San Benito, water recoveries may have to be lowered due to excessive scaling.

9.2. Lessons Learned

This project has demonstrated the need for well-coordinated inter-agency and agency-consultant collaborations. The major "lessons learned" are listed below:

1. Regulatory requirements for discharging combined RO effluent (brine plus product water) are important, even at the pilot scale. The requirement for continuous monitoring of the combined plant necessitated plant modifications.
2. Membrane cleaning produces large quantities of chemicals that need to be disposed according to strict hazardous waste disposal regulations. Disposal of membrane cleaning wastes needs to be considered at the planning stage of the project and costs need to be factored into O&M costs.
3. The reliability of the power supply is critically important. Power failures caused by rainstorms led to severe fouling events that required time-consuming system cleanings. To protect against the consequences of power failur3 months cleaning cycles es, the pilot system was retrofitted with an automatic flush cycle that was activated upon a sudden loss of power.
4. All-weather access to the pilot-plant sites by car is a critical site requirement. Periods of heavy rain softened the soil and prevented access to the San Benito site by motor vehicles.
5. Daily visits by the operators are necessary. Although important functions of the pilot plant were automated and the data acquisition system was observable via the internet, it was necessary to visit the systems on a daily basis for minor flow adjustments.
6. The complexities and challenges of operating RO pilot systems in remote locations require significant local support, most importantly for supplying water and disposing the brine and spent cleaning solutions, and providing infrastructure. Without such support, this project could not have been executed.

9.3. Recommendations

1. To operate at 83% water recovery, treatment conditions need further optimization. An option is to treat water with lower TDS values or operate at a lower water recovery (e.g., 75% or less).
2. Lowering water recovery or treating lower TDS source water may affect the economic evaluation and possible process schemes.
3. Further studies are needed to quantify biological fouling and the role that antiscaling agents can play and the optimal antiscaling agent usage. Knowing the fouling mechanism in greater detail would allow plant operators to optimize the antiscaling agent additions and fouling protocols.
4. Groundwater desalinization and the remediation of saline aquifers represent extraordinary challenges that have received relatively little consideration in the literature. Development of optimal desalinization strategies requires careful consideration of brine disposal options but also local hydrological and geochemical conditions.
5. Recovery and fouling studies need to be conducted at groundwater sites with higher TDS concentrations to validate RMC's cost evaluations.

10. Glossary

ACWD Alameda County Water District
AMI Applied Membrane Inc.
DRIP Desalination Research and Innovation Partnership
DWR Department of Water Resources
EDC endocrine disrupting compound
EPA/USEPA United States Environmental Protection Agency
GW groundwater
HUAWWMP: Hollister Urban Area Water and Wastewater Master Plan
MMWD Marin Municipal Water District
MTR Membrane Technology and Research, Inc.
RO Reverse Osmosis
SBCWD San Benito County Water District
SCVWD Santa Clara Valley Water District
PVWMA Pajaro Valley Water Management Agency
STD Standard deviation
TDS: total dissolved solids
VSEP: Vibratory Shear Enhanced Process

11. Units of Measurement

AF: acre-feet
AFY: acre-feet per year
Gal: gallon
GPM: gallons per minute
HP horsepower
PSI: pounds per square inch

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Appendices

Appendix A: AMI System Proposal.

Appendix B: Schematic of RO System

Appendix C: Pictures of RO system at Gilroy.

Appendix D: Product description, Material Safety Data Sheets, and cleaning protocols

Appendix E: Analytical methods used for membrane autopsy and trace organic analysis

Appendix F: Laboratory reports

Appendix G: Modeling RO rejection and scaling using the ROSA software package